

TA 490
.H3

ALLOYS OF CHROMIUM, COPPER AND NICKEL

BY

OSCAR EDWARD HARDER

B. A. University of Oklahoma, 1910

M. A. University of Oklahoma, 1911



Thesis submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy in Chemistry in
the Graduate School of the University of Illinois,
1915



ALLOYS OF CHROMIUM, COPPER AND NICKEL

BY

OSCAR EDWARD HARDER

B. A. University of Oklahoma, 1910

M. A. University of Oklahoma, 1911

Thesis submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy in Chemistry in
the Graduate School of the University of Illinois,
1915

[Urbana, 1917]

TA490
.H3

Gift
The University
JUL 2 1917

21

17-22101

CONTENTS

I. INTRODUCTION	PAGE
1. Purpose of the Investigation	5
2. Present state of information	5
3. Plan of Work	6
4. Summary of Results and Conclusions	6
II. PREPARATION OF THE ALLOYS	
5. Materials	8
6. Melting the Metals	9
7. Casting the Samples	10
8. Composition of the Alloys	10
9. Analysis	10
10. Changes in Composition	10
11. Alloy of 50 Per Cent Cr. and 50 Per Cent Cu.	12
III. PHYSICAL AND MECHANICAL PROPERTIES	
12. Color and Appearance	14
13. Method of Plotting Diagrams	14
14. Specific Gravity	14
15. Brinell Hardness Number	17
16. Tensile Strength and Stress Deformation Tests	18
Test Pieces	18
Testing Machine and Method of Loading	18
Extensometer	18
Calculation of Modulus of Elasticity	18
Reduction and Elongation	19
Ultimate Strength	20
Modulus of Elasticity	20
IV. CORROSION TESTS	PAGE
17. Reason for Tests	20
18. Materials	20
19. Methods	22
Solutions	22
Suspending the specimens	22
Temperature	22
Time	22
Calculations	22
Accuracy of the Method	23
20. Results	23
Nitric Acid	24
Hydrochloric Acid	26
Sulfuric Acid	26
Sodium Hydroxide	26
Ammonium Hydroxide	27
Sodium Chloride	27
Fatty Acids	27
Comparison of Corrosions	28
21. Conclusions	28
V. RELATION BETWEEN CORROSION AND RELATIVE ELECTROMOTIVE FORCES	
22. Purpose of Measurements	29
23. Method and Results of Measurements	30

VI. THERMAL ANALYSIS AND MICROSCOPIC EXAMINATION

24. Difficulties of Thermal Analysis	33
25. Heat Treatment	35
26. Microscopic Examination	35
General Discussion	35
Etching Reagents	36
Ferric Chloride and Hydrochloric Acid	36
Iodine	36
Results	
Chromium-Nickel Alloys	36
Copper-Nickel Alloys	37
Solubility of Chromium in Copper	37
Effect of Nickel on the Solubility of Chromium	37
Crystals in Nickel-rich Alloys	38
Annealing Tests	38

APPENDIX.—Historical Review

1. Copper-Nickel Alloys	52
2. Chromium-Copper Alloys	54
3. Chromium-Nickel Alloys	54
4. Ternary Alloys	57

LIST OF FIGURES

	PAGE
1. Diagrams Showing Alloys Having Possible Commercial Value.....	9
2. and 3. Microphotographs Showing Separation of Copper from Chromium in a 50 Per Cent Cu., 50 Per Cent Cr. Alloy.....	13
4. Diagram Showing Composition of Alloys and Specific Gravities at 25 C....	15
5. Stress Deformation Curves for Alloys	21
6. Diagram Showing Composition of Alloys and Corrosion in Normal Nitric Acid Solution	23
7. Diagram Showing Composition of Alloys and Corrosion in Normal Hy- drochloric Acid Solution	24
8. Diagram Showing Composition of Alloys and Corrosion in Normal Sul- furic Acid Solution	26
9. Diagram Showing Composition of Alloys and Corrosion in Normal So- dium Hydroxide Solution	27
10. Diagram Showing Composition of Alloys and Corrosion in Normal Am- monium Hydroxide Solution	28
11. Diagram Showing Composition of Alloys and Corrosion in Normal So- dium Chloride Solution	29
12. Diagram Showing Composition of Alloys and Corrosion in Fatty Acids	30
13. Diagram Showing Composition of Alloys and their Changes in Electro- motive Force in a Four Normal Sodium Chloride Solution.....	33
14. to 65. Microphotographs of the Alloys	30-51
66. Copper-Nickel Equilibrium Diagram After Tafel	53
67. Copper-Chromium Equilibrium Diagram After Hindrichs	55
68. Nickel-Chromium Equilibrium Diagram After Vöss	56

LIST OF TABLES

1. Composition of Alloys	11
2. Hardness, Specific Gravity and Kind of Castings	16
3. Hardness Test by Canada Department of Mines	17
4. Composition, Modulus of Elasticity, and Ultimate Tensile Strength of Alloys	19
5. Corrosion in Normal Nitric Acid	25
6. Comparison of the Corrosions in the Different Solutions.....	31
7. Relative Electromotive Forces of the Different Alloys in Contact with Four Normal Salt Solutions.....	34

A PRELIMINARY STUDY OF THE ALLOYS OF CHROMIUM, COPPER, AND NICKEL*

I. INTRODUCTION

1. *Purpose of the Investigation.*—The growing interest in special acid-resisting alloys and the many uses found for them has stimulated both the search for efficient materials of this nature and the study of the causes underlying their inertness. The alloys developed by Professor S. W. Parr for use in calorimeter construction have shown this quality of high resistance to corrosion to a marked degree. The almost perfect insolubility of these alloys in nitric and other acids seems to be conditioned upon a proper mixture of chromium, copper, and nickel, together with smaller quantities of such added metals as tungsten or molybdenum.†

These additions have so marked an effect in improving both the acid resisting properties and the casting qualities of the alloys that it has seemed desirable to study their effects more systematically in order that they may be used to the best advantage. The complexity of the mixtures used, however, has made the problem a very difficult one and has shown the necessity of first obtaining a more complete knowledge of the ternary alloys of chromium, copper, and nickel, and of the binary alloys of copper and nickel, copper and chromium, and chromium and nickel. With this information in hand it should be possible to understand better the effects produced by additions of a fourth metal.

In the work presented in this bulletin a preliminary survey has been made of the binary and ternary alloys and a somewhat systematic study made of their properties.

2. *Present State of Information.*—Previous investigators have studied in some detail the equilibrium conditions in the three binary systems. The freezing point curves for copper-nickel and chromium-nickel alloys have been fairly well established, but that for the chromium-copper series has been determined only in part, owing to the unusual difficulties attending the work. According to available information, these alloys belong to three different classes; copper-nickel

*The manuscript for this bulletin was originally prepared by Mr. Oscar E. Harder and submitted by him in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Illinois. Since its presentation as a thesis, it has been reviewed and in certain particulars revised by Dr. D. F. McFarland.

†S. W. Parr, *Orig. Com.* 8th Inter. Congr. Appl. Chem. Vol. 2, p. 209, 1912. Also *Jour. Am. Chem. Soc.* Vol. 37, pp. 2515-2522, 1915.

forming a continuous series of solid solutions (or mixed crystals), chromium-nickel consisting of solid solutions with a minimum point which is said to be a eutectic point, and chromium-copper having two eutectic points with a wide range in which the metals do not alloy.

The alloys of copper and nickel are commercially important in the form of Monel metal (Cu 30 per cent, Ni 70 per cent), Constantan (Cu 60 per cent, Ni 40 per cent) and other resistance alloys, and nickel coin (Cu 75 per cent, Ni 25 per cent). Chromium-nickel alloys such as "Nichrome" and similar resistance alloys have important uses. Chromium-copper alloys of a limited range of composition are also obtainable on the market. The solubility of chromium in copper has been placed at from 0.5 to 10.0 per cent by various investigators, while the solubility of copper in chromium has been placed at less than 5.0 per cent.

3. *Plan of Work.*—It was originally intended that this investigation should include the following:

a. The preparation of samples of both the binary and ternary alloys which would represent all of the possible combinations with variations of 10 per cent of the different constituents.

b. Physical and mechanical examinations which would include color, appearance, specific gravity, hardness, tensile strength, reduction of area, elongation, and modulus of elasticity.

c. Corrosion tests in solutions of nitric acid, hydrochloric acid, sulfuric acid, sodium hydroxide, ammonium hydroxide, and sodium chloride, and in fatty acids.

d. Measurements of the relative electromotive forces of the alloys in contact with salt solutions.

e. Thermal analysis and heat treatment.

f. Microscopic examination.

This program has been carried out with the exception of the thermal analysis and heat treatment. Considerable time and effort have been expended on the attempt to work out the former, but the experimental difficulties have been so great that it has been necessary to reserve this analysis for further work and future report. It was thought best also to postpone the study of heat treatment until the equilibrium diagram could be obtained.

4. *Summary of Results and Conclusions.*—The results obtained together with the conclusions drawn from them may be summarized as follows:

a. Methods have been developed for making castings of alloys of chromium, copper, and nickel; and twenty-one binary and thirty ter-

nary alloys have been prepared. From this part of the work the following conditions have been drawn.

(1) Castings of chromium and copper containing as much as 13 per cent of chromium can be prepared by melting and pouring the metals at about 1600 degrees C.

(2) Chromium-copper alloys containing 6.08 per cent or more of chromium show a separation of chromium or of a chromium-rich constituent, if they are cooled slowly.

(3) If equal weights of chromium and copper are heated together to a temperature well above the melting point of chromium and slowly cooled, the alloy is not homogeneous, but consists of two layers; the lower rich in copper, and the upper rich in chromium.

(4) The addition of nickel to alloys of chromium and copper tends to prevent the separation of the chromium or chromium-rich constituent; when the amount of nickel is more than three times the amount of copper present, the alloys become practically homogeneous.

b. Physical and mechanical tests have been made with the following results:

(1) The specific gravity at 25 degrees C. of the alloys tested varies from 8.92 to 7.89 and decreases with an increase of chromium.

(2) The Brinell hardness number varies from that of pure copper to that of tool steel and increases with an increase of chromium.

(3) The modulus of elasticity of the sixteen alloys tested varies from less than 15,000,000 to more than 40,000,000 pounds per square inch. Generally it increases with an increase of chromium.

(4) The ultimate tensile strength of the eighteen alloys tested varies from less than 10,000 to more than 50,000 pounds per square inch.

(5) The reductions and elongations are small in all cases.

(6) The stress-deformation curves are similar to those of cast iron.

c. More than three hundred corrosion tests have been made. Results show that:

(1) The amount of corrosion is not proportional to the strength of the acid or base.

(2) A triangular system of plotting shows certain fairly well-defined areas which are highly resistant to corrosion.

(3) Not only the alloys in the region approximating the composition of the alloy developed by Professor Parr are highly non-corrodible, but others have shown equally good resistance to corrosion. In general the ternary alloys are less corroded than the binary, though there are some exceptions.

d. An attempt has been made to find some relation between the relative electromotive forces obtained by placing the alloys in contact with 4 Normal sodium chloride solution and their relative resistance to corrosion, but no such relation has been found from the experimental data obtained.

e. A microscopic study of the alloys has been made and the following agreements with earlier investigators have been found:

(1) The results agree with Voss' conclusions that chromium and nickel form a series of solid solutions (mixed crystals) over the range of 100 to 50 per cent of nickel and that they form a eutectic, or, as Guertler called it, a pseudoeutectic, containing about 42 per cent of nickel.

(2) The results on the copper nickel series agree with those of Guertler and Tammann in showing a continuous series of solid solutions.

(3) All nickel-rich alloys, both binary and ternary, show well-defined polyhedral crystals.

f. In general the results indicate that the alloys of chromium-copper-nickel which show possibilities of becoming of commercial importance are limited to certain rather well-defined ranges of composition. In Fig. 1 is shown diagrammatically what seems to be the most promising field for future investigation. In the nickel-rich corner of the diagram the alloys have very large polyhedral crystals and a coarse texture, and have usually developed blow-holes in casting. There is a possibility that the texture can be improved by the addition of a fourth metal as Professor Parr has done by the use of tungsten or molybdenum. The alloys containing large percentages of chromium have such high melting points and are so hard to prepare that, unless they find special and important applications, there is little chance of their being used commercially. Alloys containing large percentages of copper with chromium show such a marked segregation that they do not machine well and their mechanical properties are poor. The region which promises best from the mechanical and physical standpoint is also, as a general rule, highly resistant to corrosion in the various solutions tested.

II. PREPARATION OF THE ALLOYS.

5. *Materials*.—All the materials used in the preparation of the different alloys were of good quality. The chromium was secured from the Goldschmidt Thermit Company and was labeled 98.99 per cent

chromium. An analysis of one sample showed 98.2 per cent chromium with the remainder consisting largely of silica, slag, etc. The nickel was C. A. F. Kahlbaum's "Nickel in Würfeln" and an analysis showed that it contained 99.6 per cent of nickel, a small amount of iron, and only a trace of cobalt. Two different lots of copper were used, both of which were electrolytic; one purchased from the J. T. Baker Chemical Company and the other from Kahlbaum.

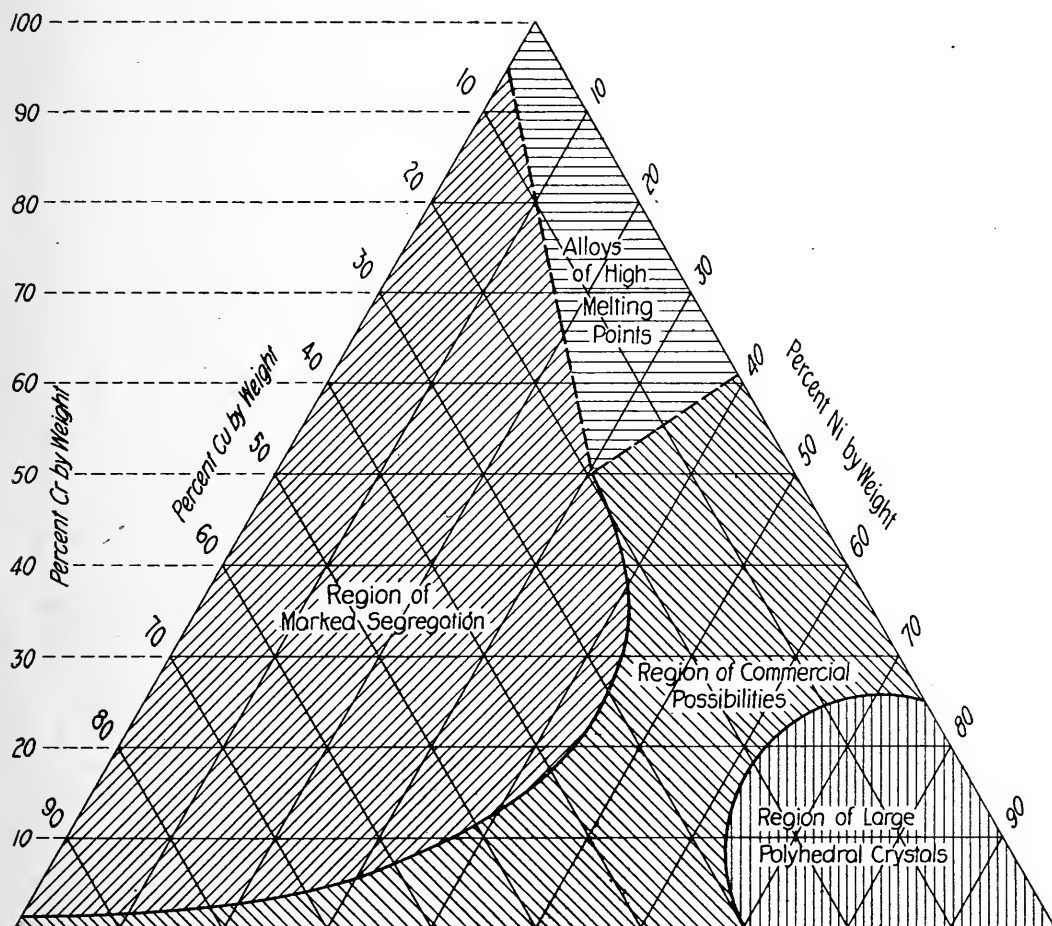


FIG. 1. DIAGRAM SHOWING ALLOYS HAVING POSSIBLE COMMERCIAL VALUES.

6. *Melting the Metals.*—The samples, with the exception of No. 1 to No. 6, inclusive, were melted in Crescent Safety crucibles in a Hoskins electric furnace of the carbon plate resistor type. These crucibles are sand crucibles covered with graphite. They withstood temperatures as high as 1600 degrees C., and in only one or two cases did they seem to be softened by that heat. It was not possible to use a crucible for more than one melt because of the corrosion of the sand lining. Samples No. 1 to No. 6, inclusive, were melted in a gas-fired

furnace in fire-clay crucibles. The metals were protected by a cover of powdered cryolite (NaAlF_4) which melted easily below the melting point of copper and effectively prevented oxidation of the chromium. It was not volatilized at the temperatures used and was the most satisfactory cover, although a number of other covers and fluxes were tried.

The charges of metals were of uniform size, 300 grams, in all cases. The furnace used from 25 to 30 kw. per hour and the time required for a melt varied from two to three hours.

7. *Casting the Samples.*—The molten metals were poured into asbestos-lined iron moulds $\frac{3}{4}$ inches in diameter and about 8 inches in length, which had been heated to a bright red temperature and packed in amorphous silica. By taking a reasonable amount of care it was possible to prevent contact of the molten alloy with the iron mould and to insure its easy removal from the mould when cold. The silica, being a good non-conductor of heat, allowed the casting to cool very slowly.

8. *Composition of Alloys.*—The intended composition of the different alloys is given in Table 1. The percentages are expressed in both atomic per cent and weight per cent. The weight per cent was calculated from the atomic per cent by means of the following formula in which *A*, *B*, and *C* represent respectively the three metals chromium, copper, and nickel.

$$\text{Weight per cent } A = \frac{\text{At. \% } A \times \text{at. wt. } A \times 100}{\text{At. \% } A \times \text{at. wt. } A + \text{at. \% } B \times \text{at. wt. } B + \text{at. \% } C \times \text{at. wt. } C}.$$

In these calculations the values $\text{Cr} = 52.00$, $\text{Cu} = 63.57$, and $\text{Ni} = 58.68$ were used as the atomic weights. Table 1 shows also the weight per cent composition of the castings found by analysis.

9. *Analysis.*—Three methods of sampling were used. For some of the softer alloys the sample was obtained by making drillings; for the specimens which were turned to test pieces the turnings were used for analysis; in all other cases a piece was taken from one end of the specimen. The copper and nickel were determined electrolytically.* Chromium was determined by precipitating it as the hydroxide, and by igniting and weighing it as the oxide. In a few cases one of the constituents was determined by difference as indicated in Table 1.

10. *Changes in Composition.*—A comparison of the composition of the charge with the composition of the casting, as found by analysis,

*The preparation of the samples for analysis and the electrolytic determination of copper and nickel in all of the alloys were done by Sydney M. Hull.

TABLE 1
COMPOSITION OF ALLOYS

Number	Atomic Per Cent Composition			Weight Per Cent Composition			Weight Per Cent Composition by Analysis		
	Cu	Cr	Ni	Cu	Cr	Ni	Cu	Cr	Ni
1	100	100.
2	90	...	10	90.71	...	9.29	90.84	...	9.06
3	80	...	20	81.27	...	18.73	81.07	...	18.76
4	70	...	30	71.65	...	28.35	71.16	...	28.46
5	60	...	40	61.90	...	38.10	61.63	...	38.25
6	50	*	50	52.00	...	48.00	48.96	...	49.90
7	40	...	60	41.94	...	58.06	69.13	...	30.59
8	30	...	70	31.70	...	68.30	41.14	...	58.27
9	20	...	80	21.31	...	78.69	20.65	...	79.35†
10	10	...	90	10.74	...	89.26	10.57	...	88.90
11	100	100.00	00.00	...	99.66
12	90	10	...	91.68	9.32	...	94.20	6.08	00.00
13	80	10	10	82.12	8.40	9.48	84.36	7.79	9.28
14	70	10	20	72.43	8.45	19.12	74.63	8.25	16.05
15	60	10	30	62.58	8.53	28.89	66.32	10.63	22.94
16	50	10	40	52.57	8.60	38.83	54.71	15.94	29.35
17	40	10	50	42.40	8.67	48.93	42.56	10.13	48.00
18	30	10	60	32.05	8.75	59.20	32.69	13.97	54.16
19	20	10	70	21.55	8.81	69.64	20.85	11.80	66.25
20	10	10	80	10.87	8.89	80.24	11.83	11.90	76.27†
21	...	10	90	...	8.96	91.04	00.00	19.37	78.99
22	80	20	...	83.02	16.98	...	87.93	13.15	00.00
23	70	20	10	73.22	17.12	9.66	80.58	10.56	9.38
24	60	20	20	63.28	17.25	19.47	56.30	14.56	29.24
25	50	20	30	53.16	17.40	29.44	66.92	13.62	19.20
26	40	20	40	42.88	17.54	39.58	44.08	19.30	36.34
27	30	20	50	32.41	17.69	49.90	36.70	15.99	47.31†
28	20	20	60	21.80	17.83	60.37	22.20	19.86	57.36
29	10	20	70	10.99	17.98	71.03	10.88	19.64	68.62
30	...	20	80	...	18.14	81.86	00.00	21.52	76.95
31	70	30	...	74.05	25.95	...	89.82	9.89	00.00
32	60	30	10	63.99	26.17	9.84	73.63	17.66	8.55
33	50	30	20	53.77	26.38	19.85	59.62	22.00	19.48
34	40	30	30	43.37	26.61	30.02	45.70	25.10	29.52
35	30	30	40	32.79	26.84	40.37	33.76	29.46	36.78†
36	20	30	50	22.05	27.06	50.89	22.58	28.10	48.42
37	10	30	60	11.12	27.29	61.59	10.90	29.70	58.12
38	...	30	70	...	27.52	72.48	00.00	28.44	71.56†
39	60	40	...	64.71	35.29	...	Not analyzed		
40	50	40	10	54.38	35.58	10.04	70.57	19.93	8.99
41	40	40	20	43.86	35.89	20.25	54.16	31.63†	14.21
42	30	40	30	33.17	36.20	30.63	33.60	38.16	26.78
43	20	40	40	22.31	36.50	41.19	22.68	41.32	34.60
44	10	40	50	11.25	36.82	51.93	11.02	43.30	46.46
45	...	40	60	...	37.14	62.86	00.00	44.93	56.55
46	50	50	...	55.20	44.80	...	Not prepared		
47	40	50	10	44.38	45.37	10.25	Not prepared		
48	30	50	20	33.57	45.76	20.67	28.42	54.92	17.12
49	20	50	30	22.58	46.16	31.26	24.12	47.54	26.28
50	10	50	40	11.39	46.56	42.05
51	...	50	50	...	46.96	53.04	00.00	57.40	41.66
52	40	60	...	44.89	55.11
53	30	60	10	33.96	55.59	10.45
54	20	60	20	22.85	56.06	21.09
55	10	60	30	11.53	56.56	31.91	Not analyzed		
56	...	60	40	...	57.07	42.93	Not analyzed		
57	30	70	...	34.37	65.63
58	20	70	10	23.13	66.21	11.56
59	10	70	20	11.66	66.80	21.54
60	...	70	30	...	67.40	32.60	Not analyzed		
61	20	80	...	23.41	76.59
62	10	80	10	11.81	77.29	10.90
63	...	80	20	...	78.00	22.00	Not analyzed		
64	10	90	...	11.96	88.04
65	...	90	10	...	88.86	11.14	Not analyzed		
66	...	100	100.00	98.21	...

*No. 6 was made up to be 50 per cent copper and 50 per cent nickel by weight.

†Determined by difference.

shows that there was a remarkable loss in chromium in the chromium-copper alloys. The highest chromium content found was in No. 22 which showed 13.15 per cent, whereas it should have shown about 17 per cent. In No. 31 the chromium should have been about 26 per cent, but analysis showed only 9.89 per cent. All attempts to prepare alloys of chromium and copper containing higher percentages of chromium failed. Even in the case of Alloy No. 12, which was slowly cooled and which contained only 6.08 per cent of chromium, there is a separation of pure chromium or of a chromium-rich constituent. (See Fig. 25.)

It has been stated by Hindrichs that at higher temperatures chromium and copper form an emulsion in which the chromium may be in a finely divided condition, and that on slow cooling the chromium collects in larger particles. It seems more probable, however, that chromium should be more soluble in copper at higher temperatures than at the melting point. In either case rapid cooling would tend to prevent such a separation and to produce a more homogeneous structure. Evidence to this effect is shown by the fact that the alloy containing 10 per cent of chromium and 90 per cent of copper which is offered for sale by the Goldschmidt Thermit Company is almost homogeneous. This alloy is said to be made by an aluminothermic method. The aluminothermic reaction produces a very high temperature, and if, as appears to be the case, the alloy is cooled suddenly, there would not be sufficient time for the separation of the chromium or chromium-rich constituent.

In the case of the other alloys there were losses of different constituents depending upon a number of conditions. In the ternary alloys rich in copper there was generally a loss in chromium, probably due to the insolubility of the chromium in the other metals present. In the ternary alloys rich in nickel and in the binary alloys of chromium and nickel, there was generally a loss of nickel, but that may be accounted for by the fact that in making up the charges precaution was taken to protect the chromium by putting it in the bottom of the crucible, thus the nickel was left more exposed to oxidation. The changes in composition may be studied in Table 1. It is certain that in making a series of alloys by such a method as has been outlined, it is not safe to assume that the composition of the alloy obtained will be the same as that of the charge melted.

11. *Alloy of 50 Per Cent Cr and 50 Per Cent Cu.*—In order to determine whether or not a homogeneous alloy containing equal parts

of chromium and copper could be prepared, the following experiments were conducted.

A charge of 30 grams of chromium and 30 grams of copper was heated in an electric furnace. A little copper was put in the bottom of the crucible, the chromium was added, and then the remainder of the copper. The charge was covered with cryolite. It was heated well above the melting point of chromium and kept at that temperature for at least fifteen minutes. The current was then shut off and the furnace allowed to cool slowly. An examination showed that the chromium had been melted. The copper which had been put on top of the charge was found at the bottom of the melt, and a fairly well defined line of separation between the copper-rich and the chromium-rich parts of the melt could be seen. (See Figs. 2 and 3.) The above experiment was later repeated with similar results. By this method it has been possible to get a division of the melt into two fairly well defined layers. From a microscopic examination (Figs. 2 and 3) it was evident that the lower layer contained some chromium, and it appeared that the upper layer contained some copper. Hindrichs stated that he was not able to get the two metals to separate into two sharply defined layers.

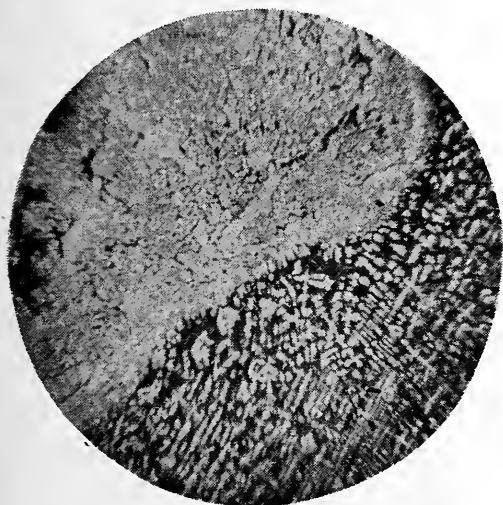


FIG. 2



FIG. 3

MICROPHOTOGRAPHS SHOWING SEPARATION OF COPPER FROM CHROMIUM IN A 50 PER CENT CU, 50 PER CENT CR. ALLOY. ETCHED IN 1 PER CENT FeCl_3 IN 1:1 HCl AND THEN STAINED IN I IN ALCOHOL. THE DARK PORTION IS THE COPPER-RICH CONSTITUENT. MAGNIFIED 30 DIAMETERS.

III. PHYSICAL AND MECHANICAL PROPERTIES

12. *Color and Appearance.*—The colors of the different alloys depend upon the amount of copper as compared with the sum of the amounts of chromium and nickel present. The chromium and nickel colors are more persistent than the copper color, and an alloy containing 50 per cent of copper and 50 per cent of nickel, or of chromium and nickel, has the color of nickel and does not show any color of copper. The alloys near the pure copper corner of the diagram (see Fig. 4) show the greatest tendency to tarnish when exposed to the air in the laboratory. On the other hand, the alloys near the nickel corner of the diagram are more porous and more likely to contain blowholes.

13. *Method of Plotting Diagrams.*—The following method has been adopted for plotting the relation between the compositions and the various properties of the alloys as shown in Fig. 4.

The three metals, chromium, copper, and nickel, are represented by the corners of the equilateral triangle. The compositions of the different alloys, as found by analysis, have been represented by the centers of the circles so that they can be read directly from the diagram. The number of the alloy has been placed inside of the circle. All of the binary alloys fall on the sides of the triangle and all of the ternary alloys fall within the triangle. One example will serve to show the method of reading the composition of the different alloys from their positions on the diagram. No. 28 is approximately on the line marked 20 per cent chromium which runs parallel to the copper-nickel side of the triangle and between the lines marked 60 and 50 per cent of nickel which run parallel to the chromium-copper side of triangle. Therefore it can be estimated that the alloy contains approximately 57 per cent of nickel. About 23 per cent is left for copper. The same result can be read from the distance of the center of the circle to the line marked 20 per cent copper which runs parallel to the chromium-nickel side of the triangle. By this method it is possible to read directly the composition of any alloy which has been plotted on the diagram. The alloys which show the copper color are Nos. 2, 3, 4, 5, 12, 13, 14, 22, 23, 31, 32, 40, and 48. Their compositions can be read from Fig. 4 or can be found in Table 1. Table 2 shows in a brief way the kinds of castings which were obtained for the different alloys.

14. *Specific Gravity.*—The specific gravities of the different alloys, as cast, are given in Table 2, and the same results are shown in Fig. 4. In the diagram the specific gravity of the alloy has been written above the circle representing the composition of the alloy.

The alloys were weighed in air and in distilled water at 25 degrees C., and the specific gravities were determined from the formula:

$$\text{Sp. gr.} = \frac{\text{Wt. in air at } t^{\circ}\text{C.} \times \text{sp. gr. H}_2\text{O at } t^{\circ}\text{C.}}{\text{Loss of wt. in H}_2\text{O at } t^{\circ}\text{C.}}$$

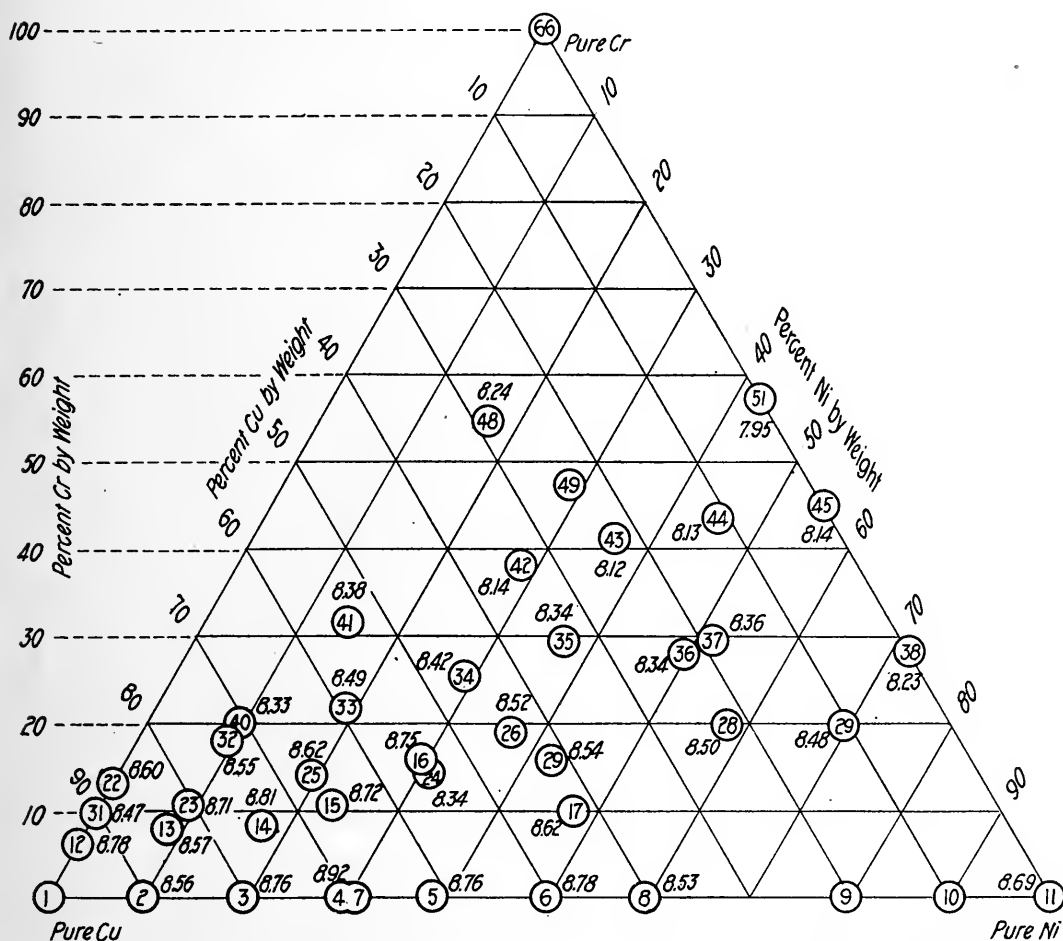


FIG. 4. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND SPECIFIC GRAVITIES AT 25 DEGREES C.

If the alloys containing a constant amount of chromium with varying amounts of copper and nickel are considered, it will be seen that there is little variation in the specific gravity. On the other hand, if the alloys containing a constant amount of copper with varying amounts of chromium and nickel are considered, it will be seen that the specific gravity decreases as the percentage of chromium increases. Similar results may be obtained if the alloys containing constant amounts of nickel and varying amounts of chromium and copper are examined. If the specific gravities are plotted as ordinates and the percentages of chromium as abscissae, fairly regular curves will be obtained. When

TABLE 2
HARDNESS, SPECIFIC GRAVITY, AND KIND OF CASTING

Number	Diameter of Impression	Brinell Hardness Number	Specific Gravity at 25° C.	Kind of Casting
1	Good.
2	Broke in test.	...	8.56	Good.
3	Cracked in test.	...	8.76	Medium.
4	Cracked in test.	...	8.92	Blowholes in places.
5	Specimen too small.	...	8.76	Blowholes in places.
6	Specimen too small.	...	8.78	Good.
7	7.20	Below 68	8.53	Good.
8	Casting had blowholes.
9	Blowholes all through.
10	Blowholes in places.
11	Broke in test. (5.4 mm. thick)	...	8.69	Large crystals and small blowholes.
12	7.20	Below 68	8.78	Good.
13	6.30	86	8.57	Sound.
14	5.80	103	8.81	Sound.
15	5.00	143	8.72	Sound.
16	4.73	161	8.75	Small, but sound.
17	4.70	163	8.62	Fair.
18	Small blowholes.
19	Fair, except for blowholes.
20	Fair, except for blowholes.
21	Large blowholes.
22	6.90	69	8.60	Sound throughout.
23	6.40	82	8.71	Good.
24	6.20	89	*8.34	Good.
25	5.90	99	8.62	Good.
26	4.80	156	8.52	Very good.
27	4.50	175	8.54	Sound.
28	4.50	179	8.50	Sound.
29	5.30	126	8.48	Sound.
30	(Specimen small)	Large blowholes.
31	7.30	68	8.47	Medium.
32	5.46	117	8.55	Small, but sound.
33	5.50	116	8.49	Excellent. There was some segregation of Cr at top of casting.
34	5.30	126	8.42	Good.
35	4.92	148	8.34	Excellent.
36	4.60	170	8.34	Excellent.
37	4.70	163	8.36	Excellent.
38	4.48	181	8.23	Good.
39	Not prepared.
40	5.40	121	8.33	Small, but sound.
41	5.50	116	8.38	Good.
42	5.20	131	8.14	Excellent.
43	4.80	156	8.12	Excellent.
44	4.70	163	8.13	Excellent.
45	4.93	147(?)	8.14	Good.
46	(Cracked in test.)
47	Not prepared.
48	5.70	107	8.24	Excellent.
49	Sound.
50	4.25	202	7.89	Good.
51	4.50	179	7.95	Good.
55	4.00	228	...	Sound.
56	4.50	179(?)	...	Sound.
60	(Specimen too small)	Sound.
63	Sound.
65	Sound.

*This value is in error because of a concealed blowhole.

the exact composition of the alloy is known, it is possible to get some idea of the relative porosity of the specimen by a study of the specific gravity.

15. *Brinell Hardness Number.*—The hardness measurements were made in the Materials Testing Laboratory of the Department of Theoretical and Applied Mechanics of the University of Illinois by using a Brinell instrument with a 3,000 kilogram load and a ball of 10 mm. diameter, the pressure being applied for 15 seconds. The diameters of the impressions were carefully measured, and the hardness numbers corresponding to those diameters were found in a table supplied by the makers of the instrument. The pieces tested had been ground smooth and were from 4 to 8 mm. thick and about 20 mm. in diameter. Only one test was made on each piece, and if it was noticed that the piece had bulged or cracked from the pressure, that fact was recorded or the results were rejected.

Specimen No. 11 requires special mention. It was a sample of pure nickel which had been melted in a magnesia crucible and slowly cooled. It had very large crystals (see microphotograph of Alloy No. 11, Fig. 24), and when a piece 5.4 mm. thick and 22 mm. in diameter was tested, it broke at a load of about 2,000 kilograms.

A comparison with the values which are given in Table 3* shows that some of the specimens were especially hard.

TABLE 3
HARDNESS TESTS BY CANADA DEPARTMENT OF MINES

Material	Date	Load	Brinell Hardness
Copper, rolled sheet, unannealed	Jan. 1913	1,000 lbs.	65.6
" " " "	" 1914	1,000 "	67.4
" " " "	" 1914	3,500 "	75.0
" " " "	" 1914	3,500 "	81.9
Swedish iron	Jan. 1913	3,500 "	90.7
" "	" 1914	1,000 "	68.6
" "	" 1914	3,500 "	75.2
Wrought iron	Jan. 1913	3,500 "	92.0
" "	" 1914	1,000 "	83.1
" "	" 1914	3,500 "	100.2
Cast iron	Jan. 1913	3,500 "	97.8
" "	" 1914	1,000 "	84.4
" "	" 1914	3,500 "	104.5
Mild steel	Jan. 1913	3,500 "	109.9
" " cold rolled shafting	" 1914	3,500 "	126.2
Tool steel	Jan. 1913	3,500 "	153.8
" " "Crescent"	" 1914	3,500 "	130.2
Spring steel	Jan. 1913	3,500 "	160.3
" "	" 1914	3,500 "	178.0
Tool steel self-hardening	Jan. 1913	3,500 "	180.0
" " " " "Rex" (before hardening)	" 1914	3,500 "	162.1
Tool steel, self-hardening	" 1914	3,500 "	240.0
" " " " "Rex" (after hardening)	" 1914	3,500 "	240.0
Tool steel, self-hardening, from work shop (School of Mines)	Jan. 1914	3,500 "	259.0
Cobalt		3,500 "	124.0

*Canada Department of Mines, Report No. 309, Part II, p. 9, by Kalmus and Harper.

It is evident that some of these alloys are as hard as tool steel, and No. 55 approaches the hardness of self-hardening tool steel after hardening. It is likely that some of the alloys in the series have still greater hardness than the one referred to since some of the others contain more chromium.

These specimens were extremely difficult to work. A saw blade was ruined on some of them without cutting more than 1 mm. deep. It has been found that by keeping the saw blades moist with turpentine they will last somewhat longer.

The results obtained by the hardness tests are shown in Table 2.

16. *Tensile Strength and Stress-Deformation Tests.*—Eighteen specimens of the alloys of various compositions were turned down to test pieces and their ultimate tensile strengths determined. In all except two cases their elongations under stresses were measured.

Test Pieces.—The test pieces which were from 3 to 4 inches in total length were turned to a diameter of approximately 0.300 inches for a length of 2.0 inches, and were threaded at the ends so that they could be screwed into half-inch grips. It was necessary to make the measurements on these short test pieces instead of the usual 8-inch specimens, because the original castings were only 4 to 5 inches long and pieces had been cut off for microscopic examination, for corrosion tests, etc. It is likely that some of the irregularities observed in the values obtained for the modulus of elasticity and for the ultimate tensile strength should be attributed to the use of the short test pieces.

Testing Machine and Method of Loading.—The testing machine on which the tests were made was an Olsen Universal Screw-Power Testing Machine of 10,000 pounds capacity. The loading was by hand and was slow except in the case of specimens No. 17 and No. 28 when the loading was done with the motor. The loading was continuous and not repeated.

Extensometer.—A Ewing extensometer having a gage of 1.25 inches was used in measuring the elongations. The instrument was sensitive and the elongations could be read accurately to 0.00008 inches and estimated to 0.000008 inches. The initial or zero extensometer reading was taken with a small load on the machine. After a satisfactory number of readings had been made the extensometer was removed and the load increased until the specimen broke.

Calculation of Modulus of Elasticity.—Curves were plotted with stresses as ordinates and elongations as abscissae. Tangents to the curves were drawn and extended to a point which corresponded to an elongation of 0.001 inch on a length of 1.0 inch, and the stress cor-

responding to that elongation was read from the cross-ruled paper. This stress minus the initial stress for zero elongation gave the modulus of elasticity. The values are given in round numbers.

The results are shown in Table 4, and the specimens have been tabulated so that the percentage of chromium increases from the top to the bottom of the column.

TABLE 4
COMPOSITION, MODULUS OF ELASTICITY, AND ULTIMATE TENSILE STRENGTH

Number	Composition of the Alloy as Found by Analysis			Modulus of Elasticity in lb. per sq. in.	Ultimate Tensile Strength in lb. per sq. in.
	Cr	Cu	Ni		
14	8.25	74.63	16.05	18,000,000	19,978
17	10.13	42.56	48.00	23,833
25	13.62	66.92	19.20	7,000,000	14,880*
24	14.56	56.30	29.24	20,000,000	17,521
26	19.30	44.08	36.34	12,000,000	14,802
28	19.64	22.20	57.36	56,255
29	19.64	10.88	68.62	7,000,000	19,846†
33	22.00	59.26	19.48	17,600,000	22,650
34	25.10	45.70	28.52	20,000,000	25,768
36	28.10	22.58	48.42	23,700,000	32,654 plus
38	28.44	71.56	15,800,000	36,958
35	29.46	33.76	36.78	16,300,000	38,734
37	29.70	10.90	58.12	22,000,000	29,630
42	38.16	33.60	26.78	26,400,000	7,449
44	43.30	11.02	46.46	16,300,000	29,587
49	47.54	24.12	26.28	43,200,000	22,336 plus
48	54.92	28.42	17.12	57,000,000	33,842†
51	57.40	41.66	48,000,000	37,200

*Showed a flaw at the fracture.

†The threads were not straight and these values are considered less reliable than the others.

The following is given as a typical set of data. The complete data for each specimen is not included.

ALLOY No. 35

DIAMETER 0.305 IN. CROSS SECTION, 0.07306 SQ. IN.

Extensometer Readings	Elongation in .0008 in.	Load in Pounds	Unit Load	Remarks
3.00	0.0000	150	2,053	
3.30	0.30	380	5,201	
3.63	0.63	625	8,554	
3.93	0.93	894	12,236	
4.23	1.23	1140	15,603	
4.55	1.55	1385	18,956	
4.83	1.83	1625	22,241	
5.18	2.18	1790	24,500	
5.60	2.60	2000	27,374	
Ultimate		2830	38,734	

Reduction and Elongation.—The per cent of reduction of area was quite small in all cases, in fact, it was so slight that measurements with a micrometer would not give appreciable decreases in diameters. The curves in Fig. 5 show that the elongations were small. These alloys

do not show well-defined yield points or elastic limits but a gradual flattening of the stress deformation curves until the ultimate is reached. The curves are similar to those for cast iron.

Ultimate Strength.—The ultimate tensile strength varied from 7,449 to 56,255 pounds per square inch cross-section. The binary alloy of chromium and nickel had more ultimate tensile strength than the ternary alloy in which 10 per cent of the nickel had been replaced by copper. (See Nos. 38 and 37.) It does not seem possible, however, to draw any general conclusions from these results as to which composition will have the greatest tensile strength. The remarkably low ultimate strength for No. 42 is probably due to the fact that it contains a large amount of chromium (38.16 per cent) and at the same time a large amount of copper (33.60 per cent), which produces an unstable condition because it has not been possible to prepare binary alloys of copper and chromium containing more than about 13 per cent of chromium.

Modulus of Elasticity.—Although there are some irregularities in the values obtained, it seems that the modulus of elasticity increases with an increase in chromium content. The values obtained vary from 15,000,000 to more than 40,000,000, or by from $\frac{1}{2}$ to $1\frac{1}{2}$ times the value for iron and steel.

A general idea of the properties of these alloys may be obtained from the stress-deformation curves which are given in Fig. 5.

IV. CORROSION TESTS

17. *Reason for Tests.*—In order to determine the power of the different alloys to resist corrosion, over three hundred tests were made. It was hoped that such a series of tests would show that some of these alloys were highly resistant to corrosion and suited for industrial purposes requiring that property.

18. *Materials.*—The corroding reagents used were normal solutions of nitric acid, hydrochloric acid, sulfuric acid, sodium hydroxide, ammonium hydroxide, sodium chloride, and molten fatty acids. The normal solutions had been carefully standardized and were known to be reasonably accurate. The fatty acids were secured from Swift & Co. of Chicago and were listed as double distilled. An analysis showed that they had a mean molecular weight of 273, an iodine value of 72, and consisted of a mixture of fatty acids. The alloy specimens used in the tests were usually about 5 mm. thick and about 15 to 20 mm. in diameter. They were ground and then polished with

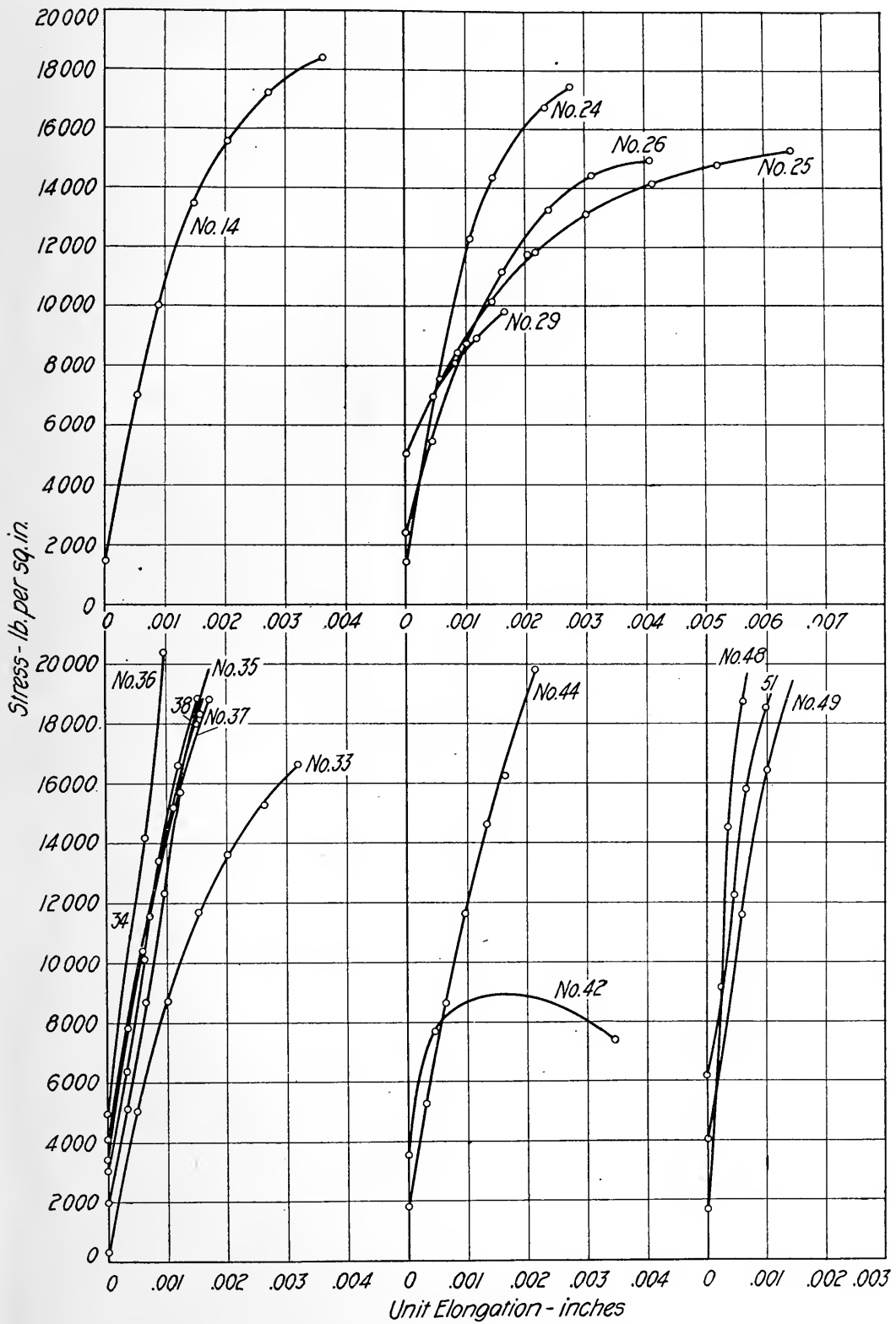


FIG. 5. STRESS DEFORMATION CURVES FOR CR-CU-NI ALLOYS.

No. 000 Hubert Emery paper. The three metals were included in the tests with the alloys. Fifty different samples were tested.

19. *Methods.*—There does not seem to be any well-established method for making corrosion tests. Different investigators have used a variety of methods. For the work in hand, the scheme used has been reasonably satisfactory and it will be described somewhat in detail.

Solutions.—In the case of the normal solutions mentioned under Section 18, 400 cc. were used for each test. No attempt was made to remove any dissolved gases, such as carbon dioxide. The solutions were contained in beakers of such size that they were filled almost to the top. Of course, the solutions changed slightly in concentration because of evaporation and of corrosion of the specimens, but that could not be avoided. The loss by evaporation was made very small by covering the beakers with watch glasses. With such a large volume of solution the change in concentration was not important in most cases. If it was observed that a specimen was dissolving very rapidly, it was removed and from the amount which had been corroded a calculation was made to find how much would have corroded in one week. One hundred grams of the fatty acids were taken for each of the tests that were made at 105 degrees C. and 200 grams for those made at 85 degrees C.

Suspending the Specimens.—Cotton thread was used to suspend the specimens in the alkaline solutions and wool thread was used in the acid solutions. The specimens were completely immersed in the liquid so that no part was in contact with the air. In some cases there was a tendency for the solutions to creep out of the beakers by way of the threads, but that was prevented by putting a little paraffin on the thread.

Temperature.—The corrosion tests were made at the temperature of the laboratory. In order to be able to approximate the mean temperature, a maximum and minimum thermometer was kept on the desk where the tests were being made and readings were taken from time to time. A calculation showed that the mean temperature for the whole period of time was 20 degrees C.

Time.—It was intended to leave the specimens in the solutions for one week, but in some cases it was necessary to remove them before the end of that period.

Calculations.—The amount of surface exposed to corrosion was determined by measuring the thickness and the diameter of the piece to the nearest 0.1 mm. and then calculating the total surface. Unless there was known to have been a big loss in corrosion, the surface was

not recalculated when the piece was used for a second test. The results have been calculated to loss in weight per week per square inch of surface exposed and have been expressed in milligrams.

Accuracy of the Method.—The accuracy of the method has not been all that might be desired. The specimens were weighed before and after the tests and the loss in weight was taken as the loss due to

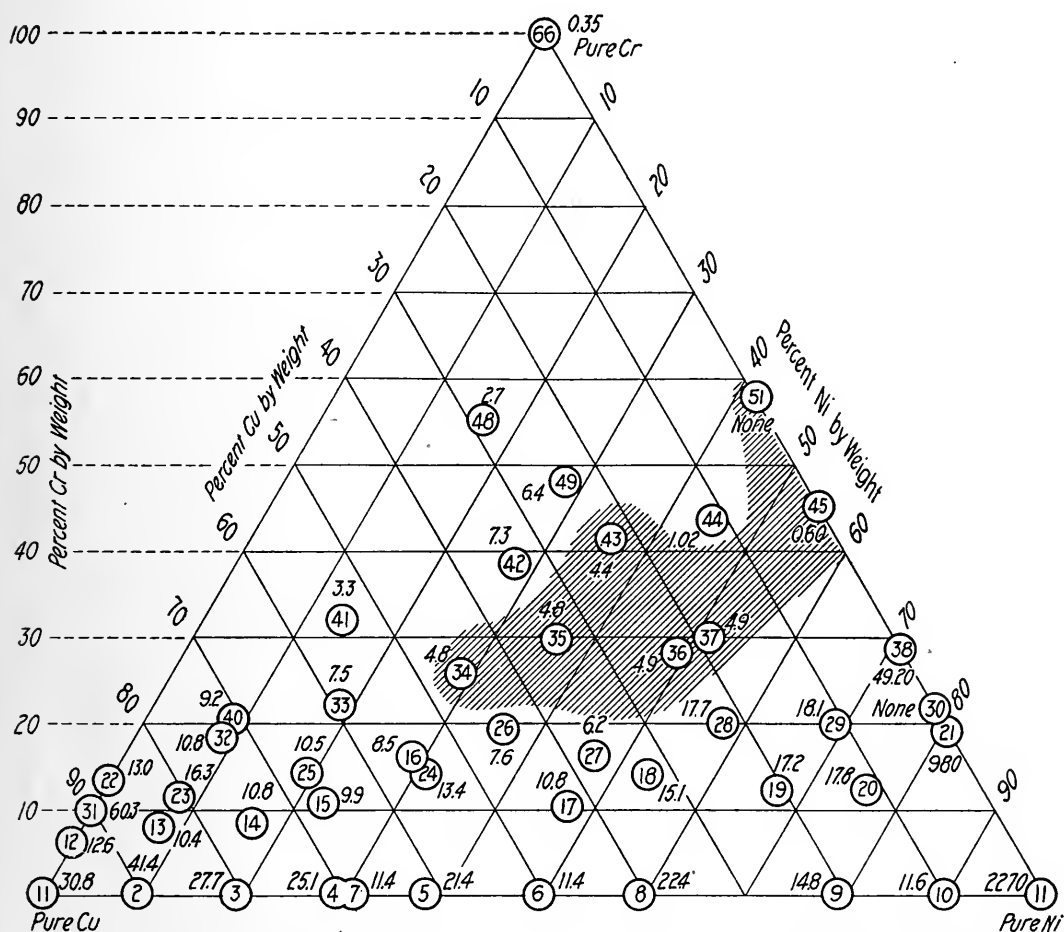


FIG. 6. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND CORROSION IN NORMAL NITRIC ACID SOLUTION.

corrosion. In a few cases a gain in weight was observed. It was hard to get all of the salts, etc. out of some of the porous pieces, but by boiling in distilled water and drying at 100 degrees C. most of that trouble was avoided. While some of the results show irregularities, as a whole they may be considered reasonably accurate and reliable.

20. *Results.*—The results of the corrosion tests are shown on triangular diagrams as explained previously (p. 14). In each diagram the loss in weight in milligrams per square inch per week for each

alloy tested is shown above the circle, the center of which represents the composition of the alloy as determined by analysis.

Complete data of the tests with normal nitric acid are given in Table 5, and by comparison of this table with the corresponding diagram (Fig. 6), the method of plotting can be readily understood. Such detailed data has been omitted for the tests with other solvents, the results being shown only in the graphical form. Areas of minimum corrosion are designated on the diagrams by shading.

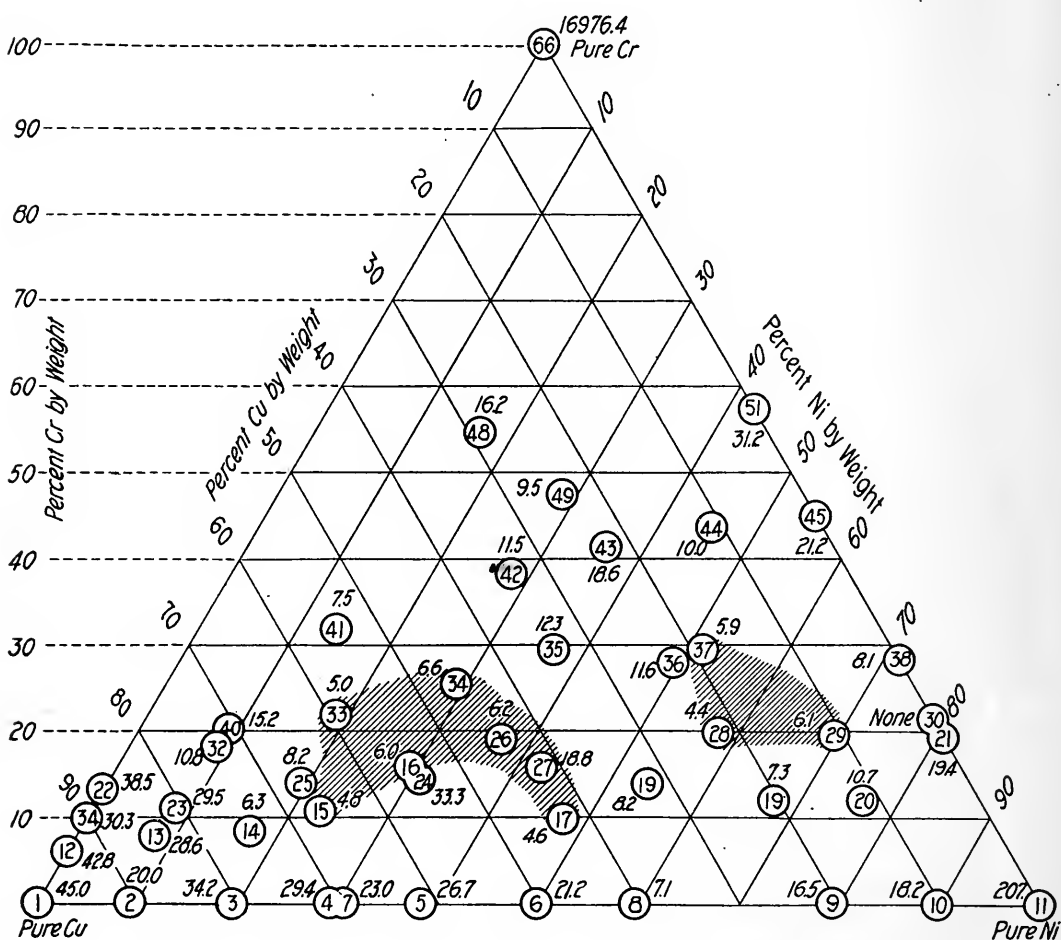


TABLE 5
CORROSION IN NORMAL NITRIC ACID

Number	Weight Before	Weight After	Loss in weight mg.	Surface		Time in solution hrs.	Loss in wt. in mg. per wk.	
				sq. in.	sq. cm.		sq. in.	sq. cm.
1	5.5125	5.4945	18.0	0.71	4.58	138	30.80	4.78
2	8.6232	8.5882	35.0	1.03	6.67	138	41.40	6.42
3	5.6478	5.6323	15.5	0.68	4.41	138	27.70	4.30
4	4.5331	4.5205	12.6	0.61	3.95	138	25.10	3.38
5	4.5007	4.4898	10.9	0.64	4.12	138	21.40	3.33
6	4.5918	4.5859	5.9	0.63	4.04	138	11.40	1.77
7	16.9032	16.8890	14.2	1.52	9.83	138	11.40	1.77
8	11.3342	11.3092	25.0	1.36	8.77	138	22.40	3.47
9	9.8259	9.8086	14.5	1.28	8.27	138	14.80	2.13
10	10.0842	10.0724	11.8	1.24	7.98	138	11.60	1.80
11	9.8700	9.4410	429.0	1.32	8.49	24	2270.00	352.00
12	11.7920	11.7783	13.7	1.33	8.58	137	12.60	1.98
13	13.1763	13.1647	11.6	1.35	8.69	137	10.40	1.62
14	10.0412	10.0310	10.2	1.16	7.47	137	10.80	1.67
15	8.4206	8.4123	8.3	1.03	6.66	137	9.90	1.53
16	7.3881	7.3807	7.4	1.07	6.94	137	8.50	1.32
17	12.8800	12.8684	11.6	1.32	8.51	137	10.80	1.67
18	10.5626	10.5474	15.2	1.24	7.98	137	15.10	2.33
19	14.3148	14.2931	21.7	1.54	9.92	137	17.20	2.67
20	10.6661	10.6490	17.1	1.18	7.61	137	17.80	2.76
21	13.2433	12.8326	410.7	1.47	9.43	48	980.00	152.00
22	9.0392	9.0390	10.2	1.07	6.91	122	13.10	2.03
23	9.1265	9.1151	11.4	1.03	6.67	122	16.30	2.22
24	10.5944	10.5821	12.3	1.26	8.10	122	13.40	2.08
25	11.1470	11.1376	9.4	1.23	7.92	122	10.50	1.63
26	13.1489	13.1412	7.7	1.39	8.95	122	7.60	1.18
27	9.7288	9.7222	6.6	1.08	7.00	168	6.20	0.95
28	9.8098	9.7948	15.0	1.17	7.56	122	17.70	2.74
29	8.0788	8.0655	13.3	1.03	6.65	122	18.10	2.80
30	Too many holes.							
31	11.1653	11.0955	69.8	1.16	7.46	168	60.30	9.35
32	12.1926	12.1777	14.9	1.38	8.92	168	10.80	1.67
33	9.7367	9.7270	9.7	1.29	8.33	168	7.50	1.16
34	11.6059	11.5994	6.5	1.37	8.82	168	4.80	0.74
35	8.8904	8.8847	5.7	1.18	7.62	168	4.80	0.74
36	9.6290	9.6241	5.9	1.20	7.73	168	4.90	0.76
37	10.8796	10.8738	5.8	1.31	8.43	168	4.90	0.76
38	9.2554	9.0129	242.5	1.18	7.62	70	492.00	76.00
39	Not prepared.							
40	13.7427	13.7295	13.2	1.45	9.33	168	9.20	1.43
41	11.5077	11.4963	11.4	1.37	8.83	168	8.30	1.29
42	10.1818	10.1725	9.3	1.28	8.23	168	7.30	1.13
43	11.5401	11.5341	6.0	1.35	8.70	168	4.40	0.69
44	11.8160	11.8146	1.4	1.37	8.81	168	1.02	0.16
45	10.5332	10.5325	0.7	1.16	7.46	168	0.60	0.09
46	Not prepared.							
47	Not prepared.							
48	10.7279	10.7154	12.5	1.29	8.32	168	9.70	1.50
49	9.1910	9.1854	5.6	1.21	7.81	122	6.40	0.99
50	10.4293	10.4198	9.5	1.28	8.23	168	7.40	1.15
51	12.4458	12.4458	0.0	1.42	9.19	168	0.00	0.00
55	9.7665	9.7559	10.6	1.38	8.89	168	7.70	1.19
56	8.4517	8.4513	0.4	1.14	7.33	168	0.35	0.05
66	2.0776	2.0774	0.2	0.57	3.66	168	0.35	0.05

of the alloys in the same region as may be seen by comparing microphotographs of Alloys No. 11, 21, 30, 38, and 45. (Figs. No. 24, 34, 43, 51, and 58.)

Hydrochloric Acid.—The results from these tests are shown in Fig. 7. It will be seen that all of the metals showed considerable corrosion in hydrochloric acid and that chromium was especially

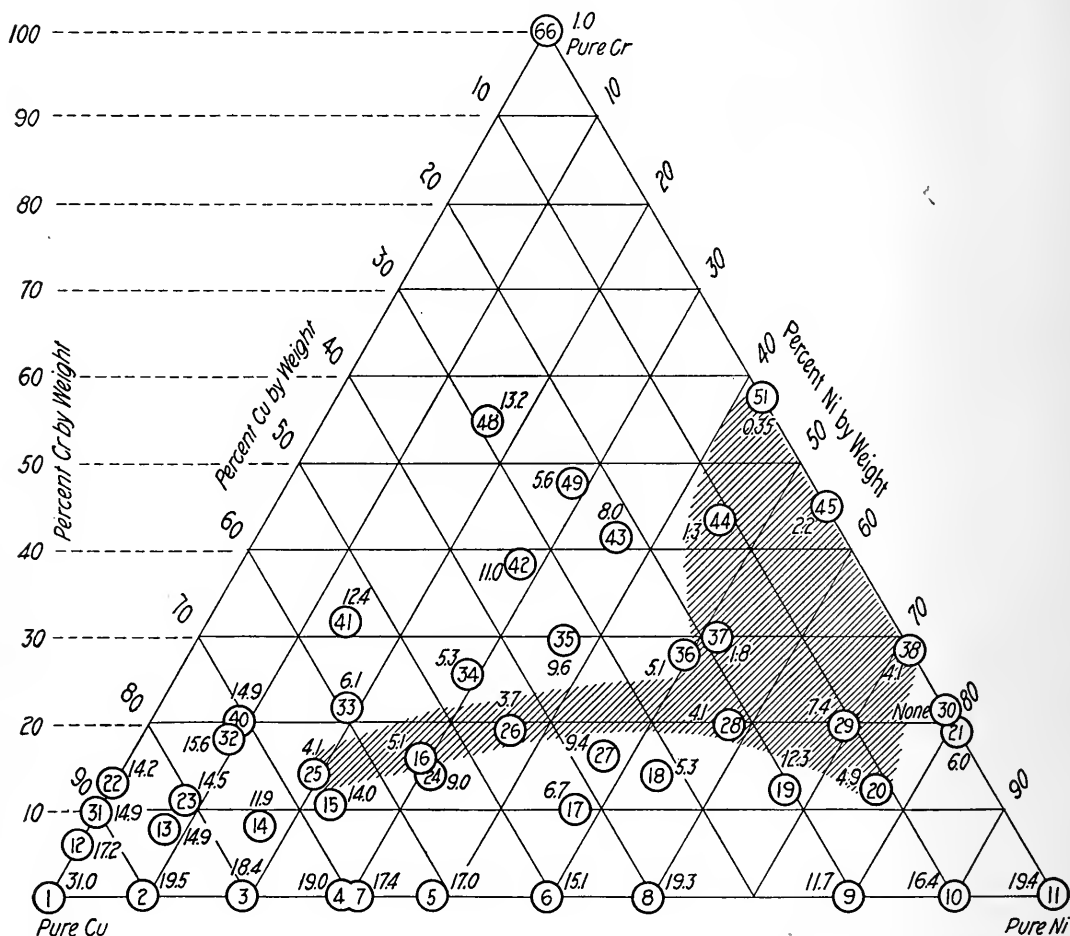


FIG. 8. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND CORROSION IN NORMAL SULFURIC ACID SOLUTION.

soluble in this acid. However, there is a fairly well-defined area in the triangle over which the corrosion was small.

Sulfuric Acid.—The data obtained from the corrosion tests in normal sulfuric acid are shown in Fig. 8. The results do not require any special explanation.

Sodium Hydroxide.—Fig. 9 shows the results obtained by the corrosion tests in normal sodium hydroxide. Copper and nickel show appreciable losses, while chromium is little attacked. In general the losses for the alloys are small.

Ammonium Hydroxide.—The alloys which best resist corrosion by ammonia are near the nickel corner of the triangle and on the chromium-nickel side. The results are shown in Fig. 10.

The copper-chromium and the copper-rich alloys show a selective corrosion in ammonium hydroxide; that is, the copper is removed

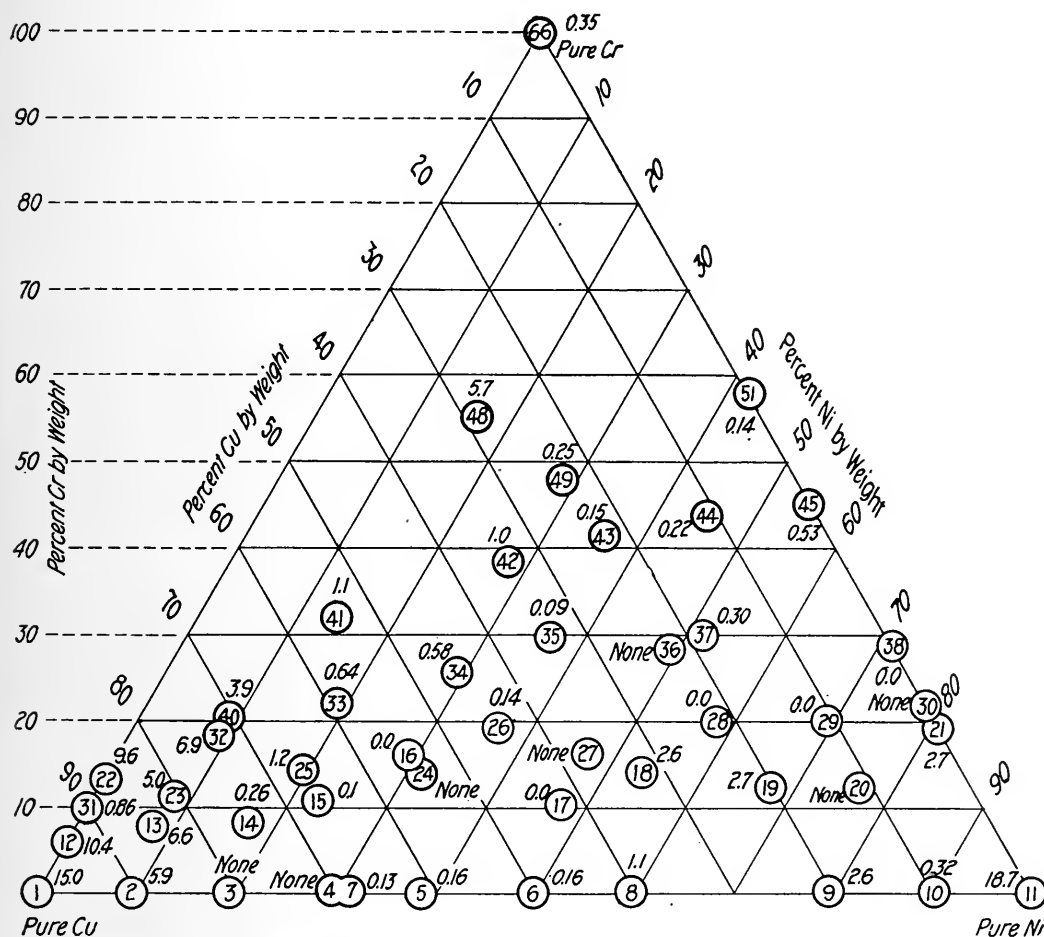


FIG. 9. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND CORROSION IN NORMAL SODIUM HYDROXIDE SOLUTION.

and some of the chromium is left. This fact suggests that good results might be obtained by using ammonia as an etching reagent in the preparation of specimens for microscopic examination.

Sodium Chloride.—Losses in normal sodium chloride solution are, in general, small. These losses are largest for alloys near the copper corner of the triangle. (See Fig. 11.)

Fatty Acids.—Only twenty-four specimens were corroded in the fatty acids. Twelve of the tests were made at 105 degrees C. by heating in an electric oven. The other tests were made at approximately

85 degrees C. by heating on a steam bath. The results are shown in Fig. 12. The greatest losses are near the copper corner of the triangle. This suggests that instead of using a copper container for fatty acids it might be advisable to use an alloy of copper and nickel, or possibly one containing copper and nickel with a little chromium.

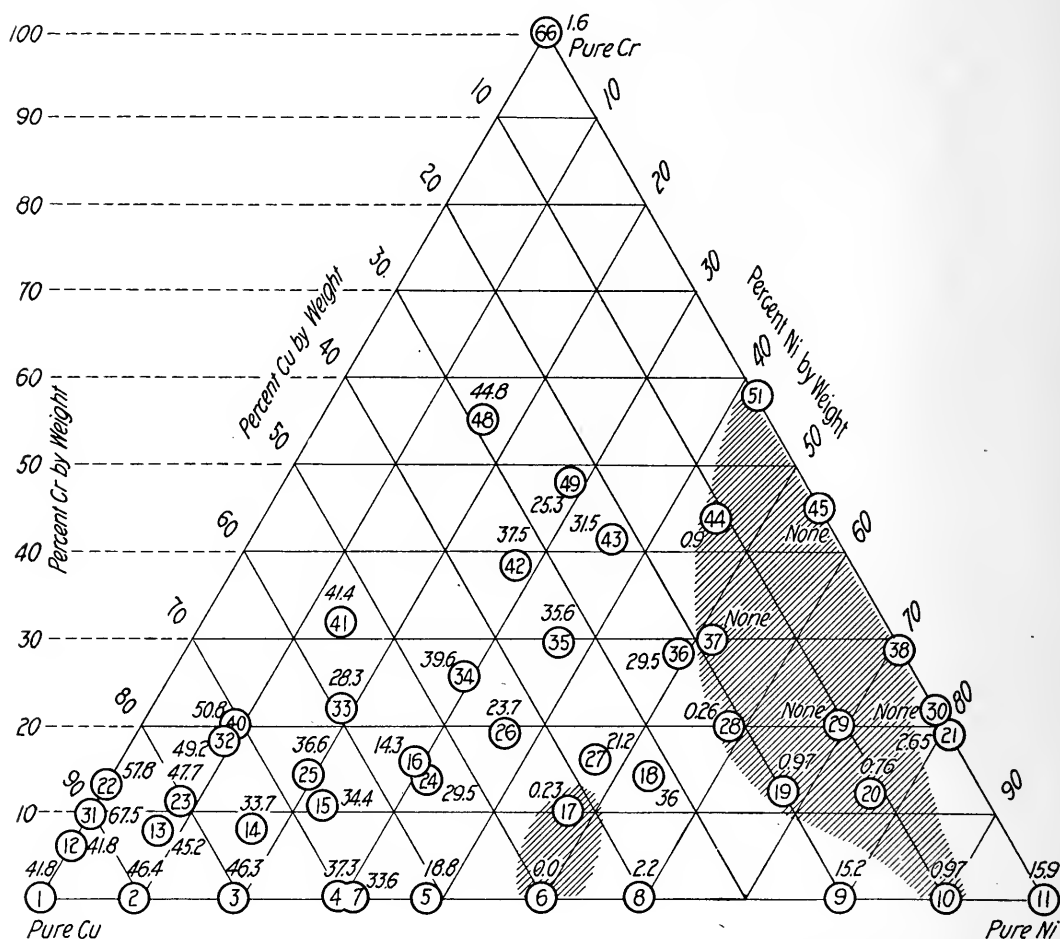


FIG. 10. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND CORROSION IN NORMAL AMMONIUM HYDROXIDE SOLUTION.

Comparison of Corrosions.—Table 6, page 31, shows the relative corrosions in the different reagents which have been used. The values are losses in weight in milligrams per square inch per week.

21. *Conclusions.*—The corrosion tests show that the amount of loss in the different reagents is not proportional to the strengths of the different acids or bases.

So far, it has not been possible to show any definite relation between the relative electromotive forces and corrosion losses.

TABLE 6

COMPARISON OF THE CORROSIONS IN THE DIFFERENT SOLUTIONS

THE VALUES ARE LOSS IN WEIGHT IN MILLIGRAMS PER WEEK PER SQUARE INCH

Number	NaCl	HCl	H ₂ SO ₄	HNO ₃	NaOH	NH ₄ OH	Fatty acids
1	5.08	45.0	31.00	30.80	15.00	41.80	8.90
2	4.18	20.0	19.50	41.40	5.90	46.40	...
3	1.60	34.2	18.40	27.70	None	46.30	5.80
4	1.65	29.4	19.00	25.10	None	37.30	...
5	2.35	26.7	17.00	21.40	0.16	18.80	2.90
6	2.37	21.2	15.10	11.40	0.16	0.00	...
7	0.78	7.1	19.30	22.40	1.10	2.20	...
8	1.71	23.0	17.40	11.40	0.13	33.60	4.00
9	1.71	16.5	11.70	14.80	2.60	15.20	...
10	1.13	18.2	16.40	11.60	0.32	0.97	...
11	None	207.0	19.40	2270.00	18.70	15.90	...
12	4.33	42.8	17.20	12.60	10.40	41.80	10.50
13	2.55	28.6	14.90	10.40	6.60	45.20	...
14	1.89	6.3	11.90	10.80	0.26	33.70	7.70
15	1.53	4.8	14.00	9.90	0.10	34.40	...
16	0.66	6.0	5.10	8.50	0.00	14.30	...
17	0.53	4.6	6.70	10.80	0.00	0.23	None
18	0.71	8.2	5.30	15.10	2.60	3.60	...
19	0.63	7.3	12.30	17.20	2.70	0.97	1.14
20	0.60	10.7	4.90	17.80	None	0.76	...
21	None	19.4	6.00	980.00	2.70	2.65	...
22	4.00	38.3	14.20	13.10	9.60	57.80	...
23	3.65	29.5	14.50	16.30	5.00	47.70	6.40
24	0.76	33.3	9.00	13.40	None	29.50	...
25	2.13	8.2	4.10	10.50	1.20	36.60	6.60
26	0.94	6.2	3.70	7.60	0.14	23.70	3.80
27	0.85	18.8	9.40	6.20	None	21.20	0.87
28	0.37	4.4	4.10	17.70	0.00	0.26	...
29	0.51	6.1	7.40	18.10	0.00	0.00	0.25
30	Too many blowholes.						
31	4.60	30.3	16.40	60.30	0.86	67.50	10.70
32	3.30	10.8	15.60	10.80	6.90	49.20	...
33	2.62	5.0	6.10	7.50	0.64	28.30	7.50
34	1.37	6.6	5.30	4.80	0.58	39.60	...
35	1.05	12.3	9.60	4.80	0.09	35.60	3.80
36	0.37	11.6	5.10	4.90	None	29.50	...
37	...	5.9	1.80	4.90	0.30	None	...
38	0.37	8.1	4.10	492.00	0.00	None	8.30
39	Not prepared.						
40	2.95	15.2	14.90	9.20	3.90	50.80	11.30
41	1.84	7.5	12.40	8.30	1.10	41.40	...
42	1.67	11.5	11.00	7.30	1.00	37.50	2.90
43	1.25	18.6	8.00	4.40	0.15	31.50	...
44	0.45	10.0	1.30	1.02	0.22	0.90	0.34
45	0.40	21.2	2.20	0.60	0.53	0.00	...
46	Not prepared.						
47	Not prepared.						
48	2.45	16.2	13.20	9.70	5.70	44.80	3.25
49	0.87	9.5	5.60	6.40	0.25	25.30	...
50	0.37	19.5	6.40	7.40	1.00	0.90	2.40
51	0.27	31.2	0.35	0.00	0.14	0.00	...
55	0.33	11.9	3.70	7.70	1.00	0.20	...
56	0.27	32.2	1.30	0.35	0.44	0.50	...
66	2.00	16976.4	1.00	0.35	0.35	1.60	1.23

In all cases there are certain fairly well-defined ranges of composition as shown in the diagrams in which the alloys are highly resistant to corrosion.

Generally the ternary alloys are less corroded than the binary, though there are some exceptions.

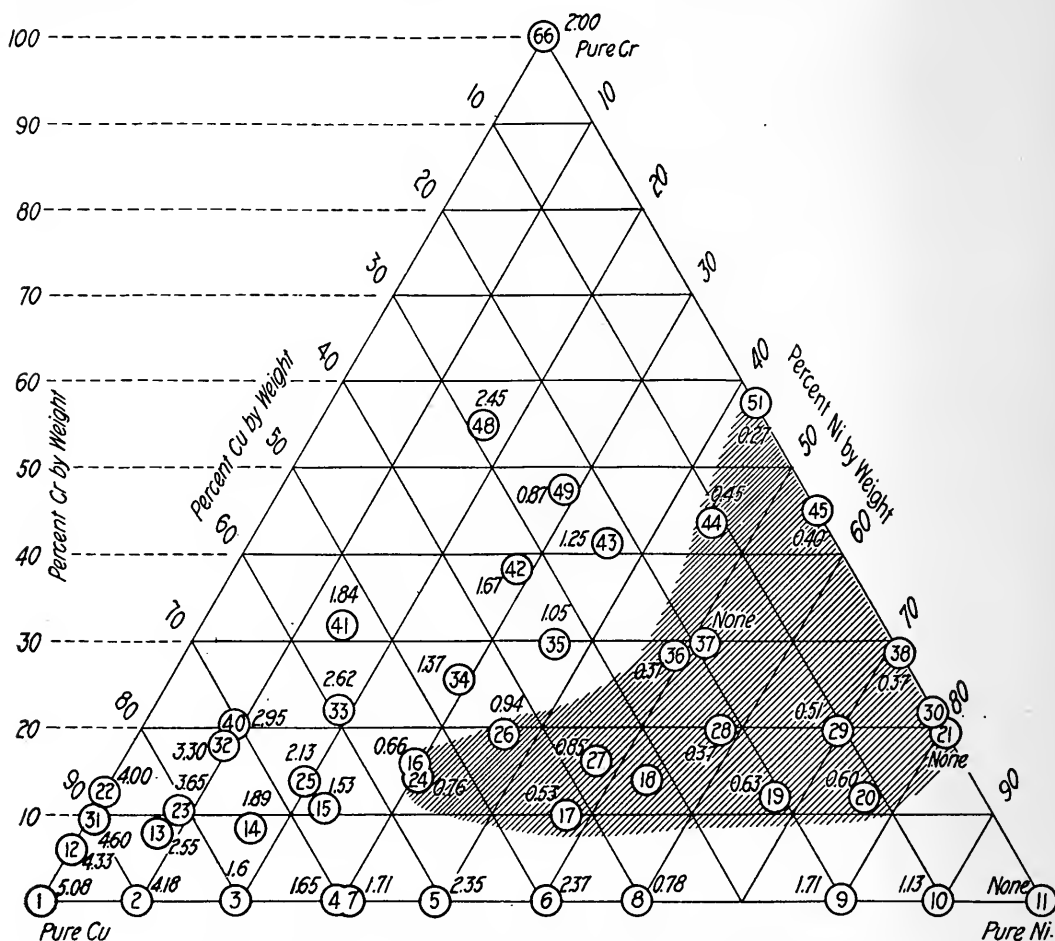


FIG. 11. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND CORROSION IN NORMAL SODIUM CHLORIDE SOLUTION.

V. RELATION BETWEEN CORROSION AND RELATIVE ELECTROMOTIVE FORCES

22. *Purpose of Measurements.*—A series of measurements was made of the relative electromotive forces developed by the different alloys when placed in contact with an electrolyte, to ascertain whether or not any simple relation could be found between the values obtained and the amount of corrosion sustained by the same alloys in the same electrolyte. The measurements were made in a sodium chloride solution and the data obtained is of considerable interest, but it is not sufficient to afford a basis for any general conclusions.

These values are not absolute, but relative, for they were made under the same conditions. The following factors seemed to influence the results: (a) The condition of the specimen as regards polishing. (b) The depth to which the piece was immersed in the solution. The latter factor was active until the piece was at least one-half covered; after that the value did not seem to change even upon complete immersion. (c) The time that the solution and specimen were left in contact, especially if any current was allowed to flow through the system. It is believed that this effect was caused by the deposition of gases upon the specimen or possibly by gases already dissolved in them. (d) Any moving of the specimen or solution.

It was noticed that the alloys which contained high percentages of copper gave values which increased with time, whereas those containing high percentages of nickel gave values which decreased with time. These results together with the composition of the alloys are shown diagrammatically in Fig. 13. Those alloys which showed an increase have been marked with a plus sign and those which showed a decrease have been marked with a minus sign. Alloys Nos. 17, 18, and 19 seem irregular, but they contained blowholes; and if there was any concentration of the low melting constituent (copper) at the blowholes, it might be expected that they would behave like the copper-rich alloys. No. 24 is the only one which did not show a change in the five minute interval, although the changes shown by some of the others were very small. From an examination of the corrosion tables it may be seen that the alloys which showed little or no change in relative electromotive force were not immune to corrosion in the different solutions. Therefore, it does not seem that resistance to corrosion can be predicted from the fact that the relative electromotive force of the alloy in contact with an electrolyte either remained constant or showed little variation.

In the case of the corrosions in normal salt solutions it was noticed that, almost without exception, the alloys which had shown an increase in the relative electromotive force were the ones which showed a turbidity of the corroding solution, while those which had given decreasing values remained clear. Similarly, in the corrosions in ammonium hydroxide the solutions were colored a deep blue in the case of the alloys which had shown increases in the relative electromotive forces, while the others remained practically colorless. However, when the corrosion specimens were weighed, it was found that there had been losses in the salt solutions, which had remained clear,

and in the ammonium hydroxide solutions, which had remained colorless.

From the results obtained it is not felt that any safe conclusions can be drawn as to the possibility of predicting the corrodibility of an alloy from such a series of measurements of the relative electromotive forces or from the changes in these values with time.

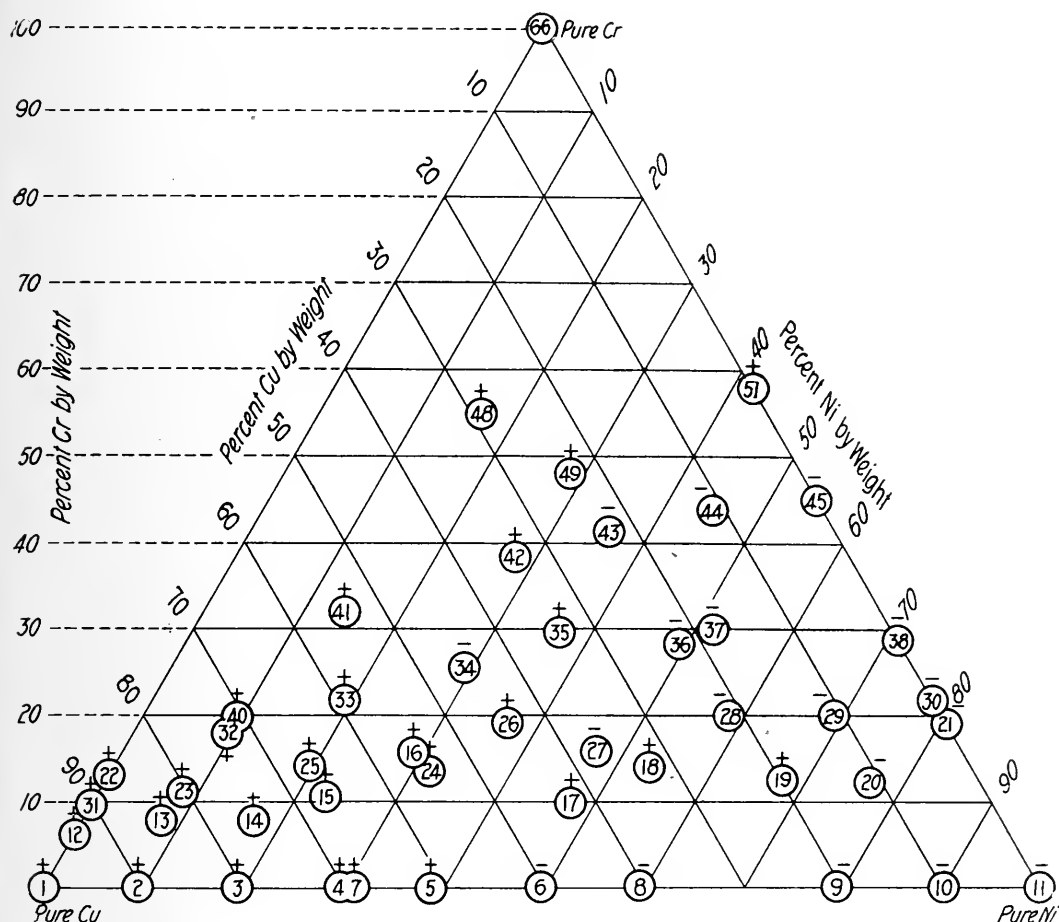


FIG. 13. DIAGRAM SHOWING COMPOSITION OF ALLOYS AND THEIR CHANGES IN ELECTROMOTIVE FORCE IN A 4 NORMAL SODIUM CHLORIDE SOLUTION.

VI. THERMAL ANALYSIS AND MICROSCOPIC EXAMINATION.

24. *Difficulties of Thermal Analysis.*—The very high melting points of the metals and alloys of this system, their great susceptibility to oxidation and absorption of impurities at high temperatures, and the extreme difficulty of finding suitable materials for pyrometers, tubes, and crucibles, all combined to make the study of freezing point curves extremely difficult, and, so far as present developments are concerned, almost impossible.

TABLE 7

RELATIVE ELECTROMOTIVE FORCES OF THE DIFFERENT ALLOYS IN CONTACT WITH
4 NORMAL SALT SOLUTIONS

Number	Relative Electromotive Force After						Change	Remarks
	1 min.	2 min.	3 min.	4 min.	5 min.			
1	0.364	...		Increasing
2	0.328	0.328	0.334	0.331	0.331	+ .003		
3	0.328	0.330	0.331	0.333	0.334	+ .006		
4	0.311	0.316	0.317	0.318	0.319	+ .009		
5	0.314	0.318	0.315	0.318	0.315	+ .001		
6	0.309	0.302	0.296	0.295	0.293	— .016		
7	0.313	0.315	0.315	0.318	0.318	+ .005		
8	0.305	0.300	0.300	0.297	0.296	— .009		
9	0.295	0.295	0.290	0.280	0.280	— .015		
10	0.318	0.309	0.300	0.294	0.289	— .029		Pure nickel
11	0.294	0.294	0.290	0.287	0.287	— .007		
12	0.338	0.341	0.345	0.346	0.348	+ .010		
13	0.345	0.343	0.348	0.348	0.350	+ .005		
14	0.340	0.341	0.341	0.339	0.339	— .001		
15	0.348	0.345	0.344	0.342	0.341	— .007		
16	0.342	0.336	0.333	0.332	0.330	— .012		
17	0.310	0.309	0.306	0.306	0.304	— .006		
18	0.307	0.304	0.303	0.303	0.303	— .004		
19	0.306	0.312	0.315	0.316	0.318	+ .012		
20	0.331	0.325	0.315	0.309	0.300	— .031		
21	0.294	0.282	0.279	0.276	0.275	— .019		
22	0.357	0.360	0.363	0.363	0.363	+ .006		
23	0.345	0.347	0.348	0.349	0.349	+ .004		
24	0.307	0.306	0.307	0.307	0.307	+ .000		
25	0.315	0.319	0.322	0.324	0.325	+ .010		
26	0.336	0.339	0.339	0.339	0.339	+ .003		
27	0.330	0.326	0.320	0.320	0.320	— .010		
28	0.355	0.344	0.339	0.332	0.330	— .025		
29	0.360	0.349	0.341	0.338	0.332	— .028		
30	0.325	0.320	0.329	0.331	0.324	— .001		
31	0.339	0.340	0.345	0.346	0.349	+ .010		
32	0.330	0.337	0.339	0.340	0.341	+ .011		
33	0.341	0.347	0.346	0.346	0.346	+ .005		
34	0.340	0.339	0.339	0.338	0.338	— .002		
35	0.333	0.333	0.334	0.334	0.334	+ .001		
36	0.334	0.330	0.329	0.320	0.320	— .014		
37	0.332	0.330	0.320	0.319	0.315	— .017		
38	0.316	0.310	0.305	0.300	0.296	— .020		Not prepared
39		
40	0.342	0.346	0.352	0.355	0.355	+ .013		
41	0.350	0.351	0.352	0.355	0.355	+ .005		
42	0.331	0.335	0.339	0.339	0.339	+ .008		
43	0.366	0.365	...	0.350	0.346	— .020		Not prepared
44	0.314	0.300	0.290	0.286	0.286	— .028		
45	0.322	0.315	0.309	0.302	0.300	— .022		
46		
47		
48	0.338	0.345	0.349	0.351	0.350	+ .012		Not prepared
49	0.345	0.347	0.349	0.349	0.349	+ .004		
50	0.298	0.299	0.298	0.295	0.295	— .003		
51	0.468	0.473	0.476	0.480	0.480	+ .012		

Note: The other specimens have either not been prepared or have not been tested.

The handicaps were overcome in part by the construction of a specially designed granular carbon resistance furnace which gave sufficiently high temperatures for the melting of the alloys. Fairly satisfactory crucibles were made of fused magnesia, which material served also as a satisfactory refractory for parts of the furnace. By means of these crucibles, melts of about 200 grams could be made.

The greatest difficulty, however, was encountered in attempting to find a protecting tube for the thermo couple which would withstand the severe conditions to which it would be exposed. Quartz tubes are good for low temperatures, but they cannot be used at the melting point of chromium. Porcelain tubes, such as were used by Hindrichs, stand slightly higher temperatures than quartz without softening, but they break easily and are attacked by chromium. An attempt was made to use an alundum tube, but it broke in the first melt. Since it was known that the fused magnesia crucibles were little attacked by chromium, it was thought that an insulating tube of the same material might be satisfactory. Some tubes were moulded, dried, and heated to about 1500 degrees C. They became hard and dense, but bent during the heating. It appears that in heating the magnesia to 1500 degrees C. it passes through a semi-fused state at which time sintering takes place, but at that same time the tubes bend so badly that they can not be used. Some magnesia tubes were moulded in which a solution of magnesium chloride was used as the binding material. These tubes, after drying at 105 degrees C., were hard and looked promising, but when heated they became brittle and crumbled to pieces at 800 to 900 degrees C. So far, all attempts to prepare satisfactory magnesia insulating tubes have failed. Because of so many difficulties and a limited amount of time, it was thought best to omit this part of the work for the time being, reserving it for later investigation.

25. *Heat Treatment*.—As was explained in the introduction it has not been considered advisable to attempt much in the way of heat treatment of the alloys until the equilibrium diagrams have been more thoroughly established.

Some annealing tests have been carried out and are mentioned at the close of this chapter.

26. *Microscopic Examination*.

a. *General Discussion*.—The metallurgical microscope used in the examination of these alloys was a Leitz "Micrometallograph." For the most part apochromatic objectives were used with projection eyepieces. Many difficulties were met with in the preparation of the

different alloys for microscopic study. No two alloys had exactly the same composition. It is almost equally true that no two of the alloys would give the best results by the same methods of polishing, etching, staining, and photographing. Thus each specimen became a research problem in itself.

b. *Etching Reagents*.—A study of the different etching reagents, stains, etc., described in the literature, was made in an endeavor to find means of identifying the different constituents in the alloys. Descriptions of the two reagents which have been found most effective follow:

Ferric Chloride in Hydrochloric Acid.—This solution consisted of 1 per cent FeCl_3 dissolved in 1:1 HCl. It has been found very useful. In some cases it was found necessary to dilute it with one or more volumes of water because the etching was too rapid. An attempt was made to secure colorations by using a mixture of 25 cc. of this solution with 25 cc. of glycerine, 2 grams of resorcin, and 50 cc. of water, but it did not give any better results.

Iodine.—Iodine has been used as the tincture and in a solution of potassium iodide. These solutions can be used to etch the specimen in some cases, but they have more value in staining the specimen after it has been etched with some other reagent. Iodine stains copper or the copper rich constituent, giving it a dark appearance; because it has little effect on either chromium or nickel, it has proved the best method for identifying the different constituents in these alloys.

Other reagents tried, but with little success, were alkaline potassium permanganate, a mixture of picric and nitric acids in amyl and ethyl alcohols, picric acid in alcohol, sodium picrate in alcohol, and tartaric acid in water.

Additional information regarding the etching and staining used may be obtained by a study of the microphotographs. (Figs. No. 14 to 65.)

c. *Results*.—Some of the results obtained from the microscopic examination have been referred to in the previous discussions. In general the data given with the microphotographs are sufficient to explain them. The composition given is in weight per cent as found by analysis, unless otherwise stated.

Chromium-Nickel Alloys.—The microscopic examination of the alloys of chromium and nickel seems to confirm Voss' conclusions:

First, that chromium and nickel form a series of solid solutions (mixed crystals) in the alloys containing from 100 to 50 per cent

of nickel. (See Figs. 24, 34, 43, 51, and 58. Alloys No. 11, 21, 30, 38, and 45.)

Second, that chromium and nickel form a eutectic which contains about 42 per cent of nickel. Guertler does not think that the metals form a true eutectic, but calls it a pseudoeutectic. Fig. 63, Alloy No. 51, is of an alloy having approximately 42 per cent of nickel and which appears to have a eutectic-like structure. Specimen No. 56, Fig. 65, which should contain more chromium, shows what appears to be the eutectic structure and an excess of chromium. Although alloys containing higher percentages of chromium have been prepared, they have not been analyzed and microphotographs of them have not been made. The reason for this has been the difficulty of cutting proper samples from the extremely hard alloys.

Copper-Nickel Alloys.—The microphotographs of the alloys of copper and nickel agree very well with those obtained by Guertler and Tammann, especially for those obtained under similar conditions; namely, with slow cooling. The alloys containing more than 80 per cent of nickel show large polyhedral crystals. Microphotographs of the pure metals and their alloys are shown in Figs. 14 to 24.

Solubility of Chromium in Copper.—The tendency for chromium or a chromium-rich constituent to separate in alloys of chromium and copper has already been discussed. This effect may be seen in Alloys Nos. 12, 22, and 31; Figs. 25, 35, and 44, and in Figs. 2 and 3. The chromium or chromium-rich constituent shows either in relief or as the light part of the photograph, if the specimen was stained with iodine.

Effect of Nickel on the Solubility of Chromium.—The effect of the addition of nickel to alloys of chromium, copper, and nickel may be studied in the microphotographs of Alloys Nos. 22 to 30, inclusive, Figs. 35 to 43, in which series there is an increase in nickel and a decrease in copper. The separation of the chromium or of the chromium-rich constituent is apparent in the Alloys Nos. 22 to 26. Those containing larger percentages of nickel are more homogeneous. In No. 29, Fig. 42, well-defined polyhedral crystals characteristic of a solid solution are shown. Similar effects will be seen if other series, such as Nos. 12 to 21, Figs. 25 to 34, and Nos. 31 to 38, Figs. 44 to 51 are studied. The alloys become practically homogeneous when the amount of nickel is more than three times the amount of copper present.

Crystals in Nickel-Rich Alloys.—It must be remembered that the alloys studied were intended to have variations of 10 per cent in their different constituents and it is not possible to say at exactly what nickel content the binary alloys begin to show well-defined polyhedral crystals. From the specimens examined, it is evident that in the case of the binary alloys those which contain as much as 80 per cent of nickel show such crystals. On the other hand, the ternary alloys show them if they contain as much as 70 per cent of nickel. Of course, the structures which have been obtained in these alloys represent what may be expected if the castings are slowly cooled, but they do not necessarily show what structure would be produced by quenching.

Annealing Tests.—Small pieces of Alloys Nos. 22 to 38, inclusive, were packed in amorphous silica in an iron pipe, $1\frac{3}{4}$ by 5 inches in dimensions and closed at both ends by caps. The pipe and contents were placed in an electric furnace and heated at a temperature of approximately 900 degrees C. for at least twenty-four hours. The specimens were repolished and examined microscopically. From a brief examination it seems that there was not any very noticeable change in the structure.



FIG. 14. ALLOY No. 1. x 40.
Cu. 100%
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

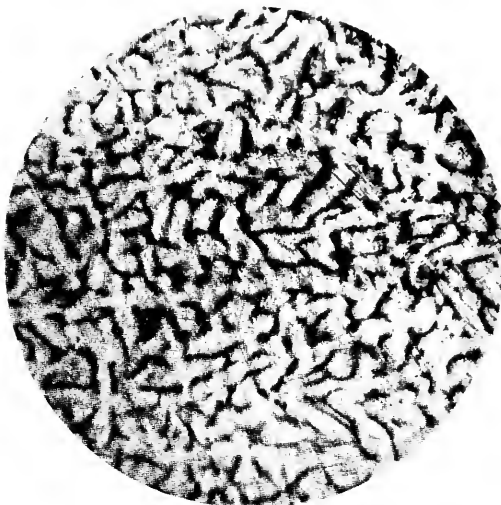


FIG. 15. ALLOY No. 2. x 40.
90.84% Cu, 9.06% Ni BY WEIGHT.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

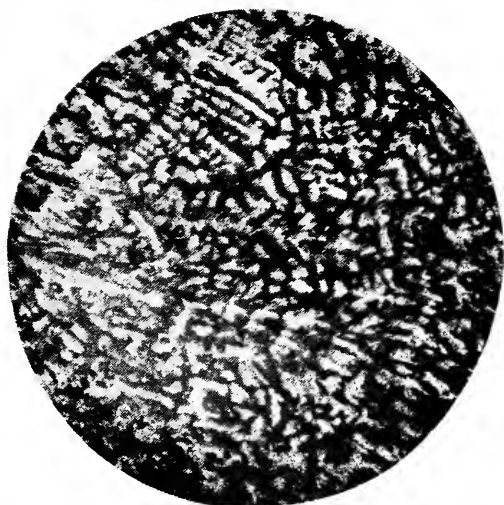


FIG. 16. ALLOY No. 3. x 40.
81.07% Cu, 18.76% Ni, BY WEIGHT.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 17. ALLOY No. 4. x 40.
71.16% Cu, 28.46% Ni BY WEIGHT.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

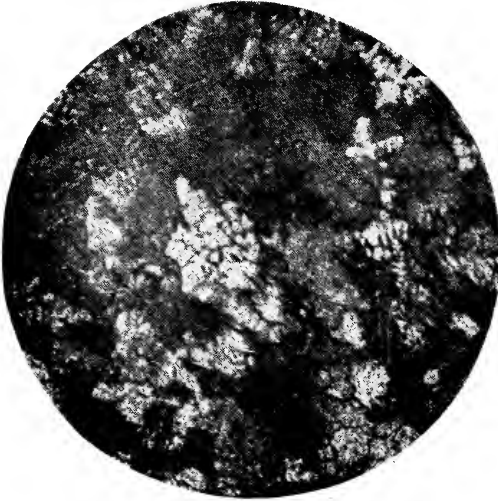


FIG. 18. ALLOY NO. 5. x 40.
61.63% CU, 38.25% NI BY WEIGHT.
ETCHED IN 1% FeCl_3 IN 1:1 HCL.



FIG. 19. ALLOY NO. 6. x 40.
48.96% CU, 49.90% NI BY WEIGHT.
ETCHED IN 1% FeCl_3 IN 1:1 HCL.

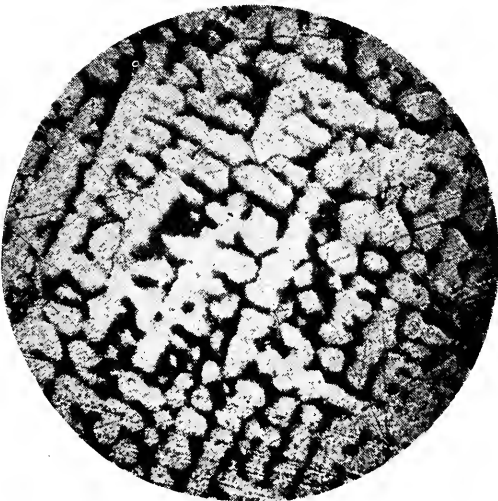


FIG. 20. ALLOY NO. 7. x 40.
69.13% CU, 30.59% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCL.

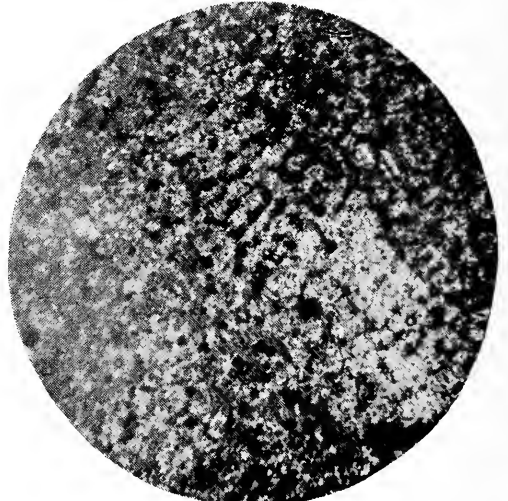


FIG. 21. ALLOY NO. 8. x 40.
41.14% CU, 58.27% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCL.



FIG. 22. ALLOY No. 9. x 40.
20.65% Cu, 79.35% Ni.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

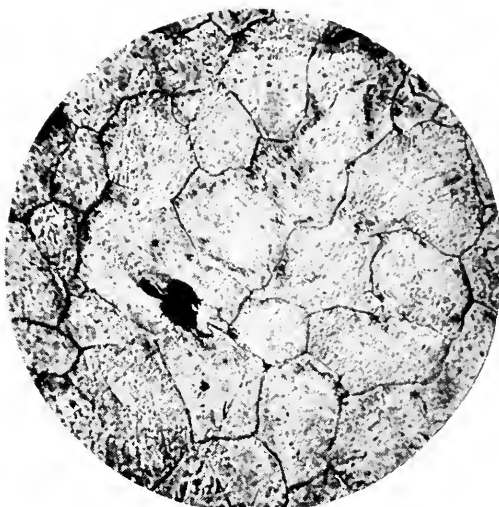


FIG. 23. ALLOY No. 10. x 40.
10.57% Cu, 88.90% Ni.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 24. ALLOY No. 11. x 40.
99.66% Ni.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

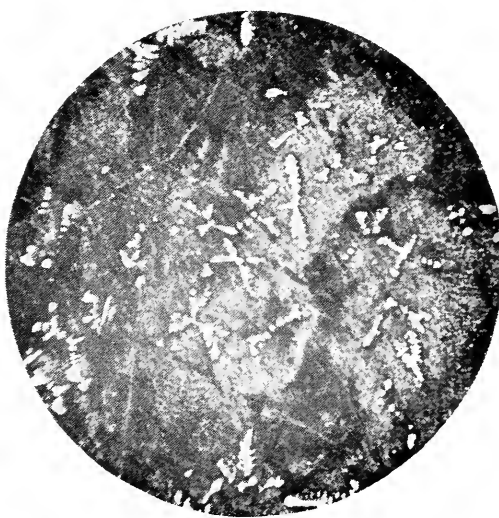


FIG. 25. ALLOY No. 12. x 40.
6.08% Cr, 94.20% Cu.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

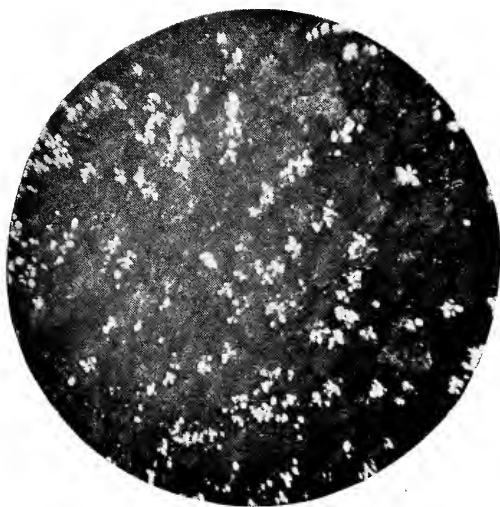


FIG. 26. ALLOY No. 13. x 40.
7.8% CR, 84.4% CU, 9.3% NI
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 27. ALLOY No. 14. x 40.
8.25% CR, 74.63% CU, 16.05% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

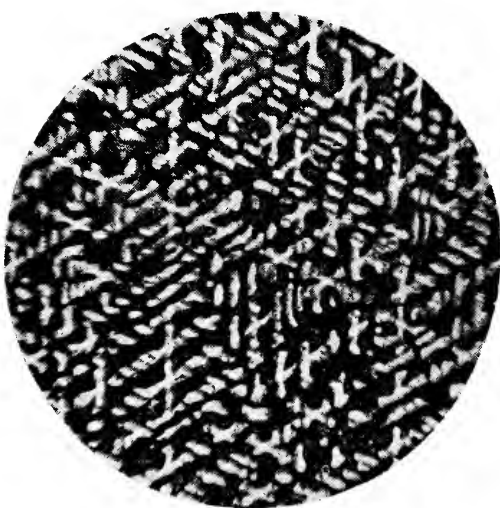


FIG. 28. ALLOY No. 15. x 40.
10.6% CR, 66.3% CU, 22.9% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 29. ALLOY No. 16. x 40.
15.9% CR, 54.7% CU, 29.4% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 30. ALLOY No. 17. x 40.
10.1% CR, 42.6% CU, 48.0% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

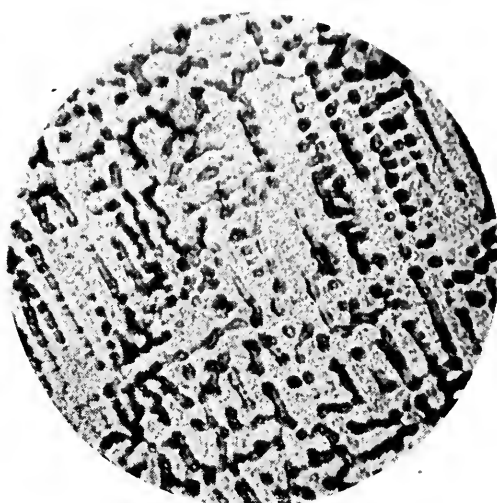


FIG. 31. ALLOY No. 18. x 40.
13.97% CR, 32.69% CU, 54.16% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 32. ALLOY No. 19. x 40.
11.80% CR, 20.85% CU, 66.25% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

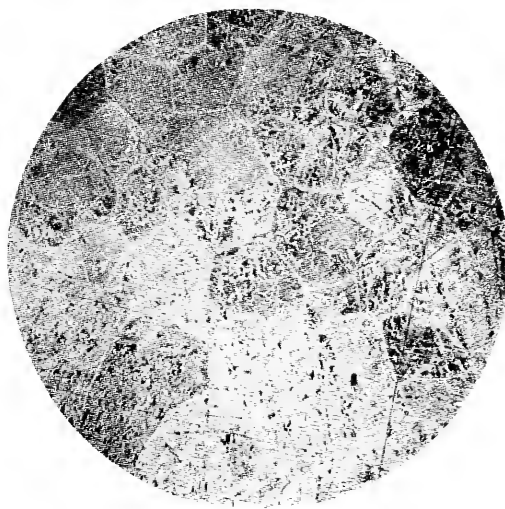


FIG. 33. ALLOY No. 20. x 40.
11.90% CR, 11.83% CU, 76.27% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

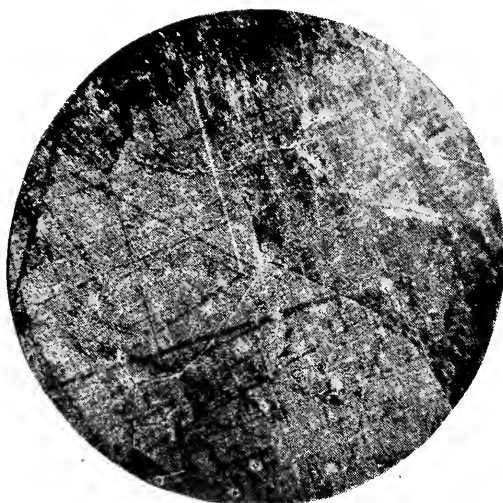


FIG. 34. ALLOY No. 21. x 40.
19.37% Cr, 78.99% Ni.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 35. ALLOY No. 22. x 40.
13.15% Cr, 87.93% Cu.
NOT ETCHED. STAINED IN I IN KI.

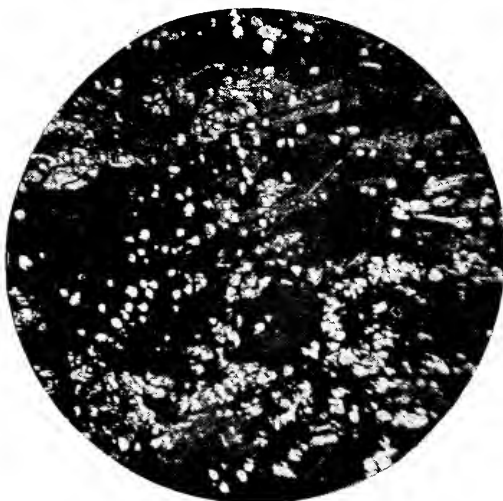


FIG. 36. ALLOY No. 23. x 40.
10.56% Cr, 80.58% Cu, 9.38% Ni.
ETCHED LIGHTLY IN 1% FeCl_3 IN 1:1 HCl.



FIG. 37. ALLOY No. 24. x 40.
14.56% Cr, 56.30% Cu, 29.24% Ni.
ETCHED AND THEN STAINED IN I IN KI.

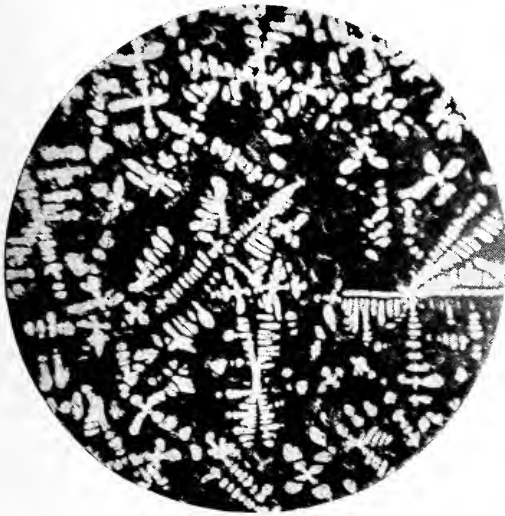


FIG. 38. ALLOY No. 25. x 40.
13.62% CR, 66.92% CU, 19.20% NI.
ETCHED AND THEN STAINED IN I IN KI.



FIG. 39. ALLOYED No. 26. x 40.
19.30% CR, 44.08% CU, 36.34% NI.
NOT ETCHED, BUT STAINED IN I IN KI.



FIG. 40. ALLOY No. 27. x 40.
15.99% CR, 36.70% CU, 47.31% NI.
STAINED IN I IN ALCOHOL.

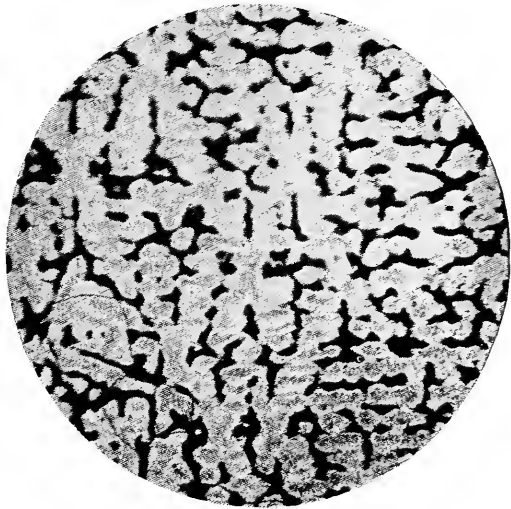


FIG. 41. ALLOY No. 28. x 40.
19.86% CR, 22.20% CU, 57.36% NI,
STAINED IN I IN ALCOHOL.

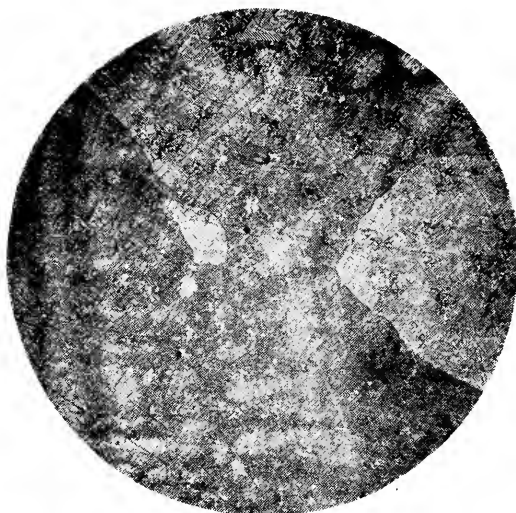


FIG. 42. ALLOY No. 29. x 40.
19.64% CR, 10.88% CU, 68.62% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 43. ALLOY No. 30. x 40.
21.52% CR, 76.95% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 44. ALLOY No. 31. x 40.
9.89% CR, 89.82% CU.
NOT ETCHED. RELIEF POLISHING.



FIG. 45. ALLOY No. 32. x 40.
17.66% CR, 73.63% CU, 8.55% NI.
NOT ETCHED. RELIEF POLISHING.



FIG. 46. ALLOY No. 33. x 40.
22.00% Cr, 59.62% Cu, 19.48% Ni.
ETCHED IN I IN KI.

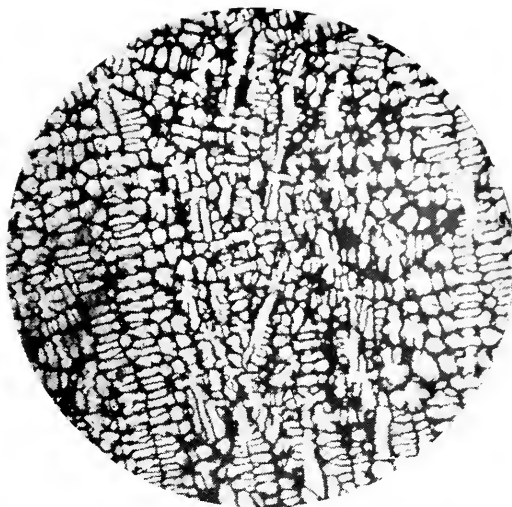


FIG. 47. ALLOY No. 34. x 40.
25.10% Cr, 45.70% Cu, 29.52% Ni.
ETCHED, THEN STAINED IN I IN KI.



FIG. 48. ALLOY No. 35. x 40.
29.46% Cr, 33.76% Cu, 36.78% Ni.
ETCHED, THEN STAINED IN I IN KI.



FIG. 49. ALLOY No. 36. x 40.
28.10% Cr, 22.58% Cu, 48.42% Ni.
ETCHED, THEN STAINED IN I IN KI.



FIG. 50. ALLOY No. 37. x 40.
29.70% CR, 10.90% CU, 58.12% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.



FIG. 51. ALLOY No. 38. x 40.
28.44% CR, 71.56% NI.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.

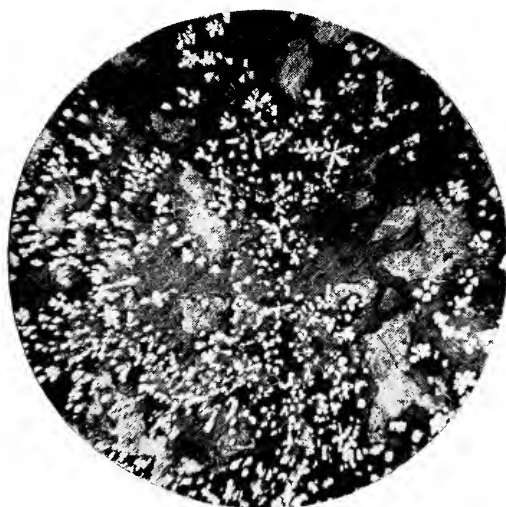


FIG. 52. ALLOY No. 39. x 40.
APPROX. 35.29% CR, 64.71% CU.



FIG. 53. ALLOY No. 40. x 40.
19.93% CR, 70.57% CU, 8.99% NI.
NOT ETCHED. RELIEF POLISHING.



FIG. 54. ALLOY No. 41. x 40.
31.63% CR, 54.16% CU, 14.21% NI.
STAINED IN I IN ALCOHOL.

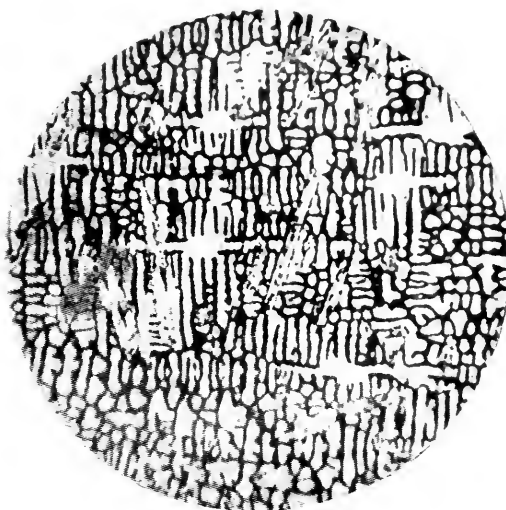


FIG. 55. ALLOY No. 42. x 40.
38.16% CR, 33.60% CU, 26.78% NI.
ETCHED, THEN STAINED IN I IN
ALCOHOL.



FIG. 56. ALLOY No. 43. x 40.
41.32% CR, 22.68% CU, 34.60% NI.
ETCHED, THEN STAINED IN I IN
ALCOHOL.

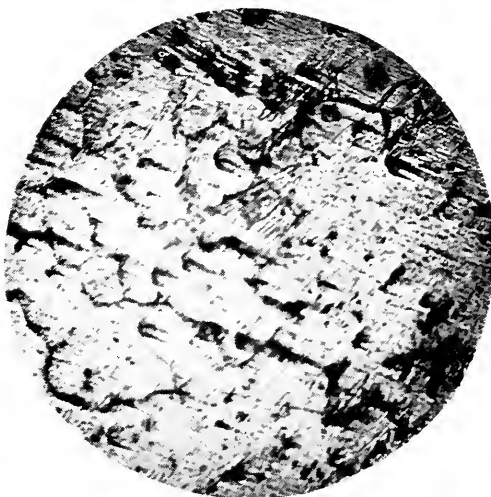


FIG. 57. ALLOY No. 44. x 40.
43.30% CR, 11.02% CU, 46.46% NI.
ETCHED, THEN STAINED IN I IN
ALCOHOL.

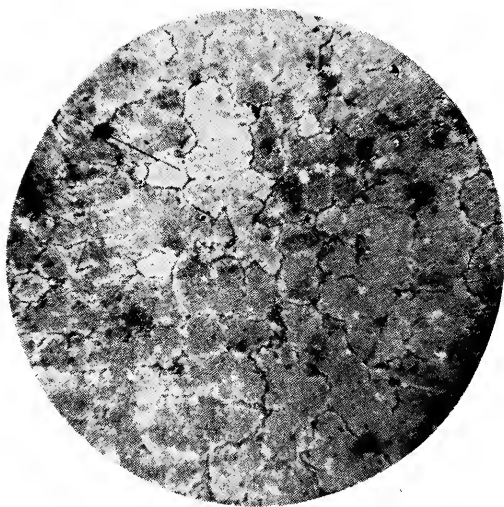


FIG. 58. ALLOY No. 45. x 40.
44.93% CR, 56.55% NI.
ETCHED IN AQUA REGIA.



FIG. 59. ALLOY No. 48. x 60.
54.92% CR, 28.42% CU, 17.12% NI.
STAINED IN I IN ALCOHOL.

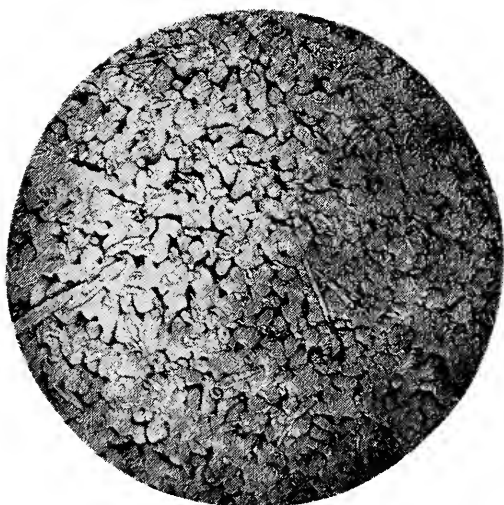


FIG. 60. ALLOY No. 49. x 40.
47.54% CR, 24.12% CU, 26.28% NI.
POLISHED. NOT ETCHED.

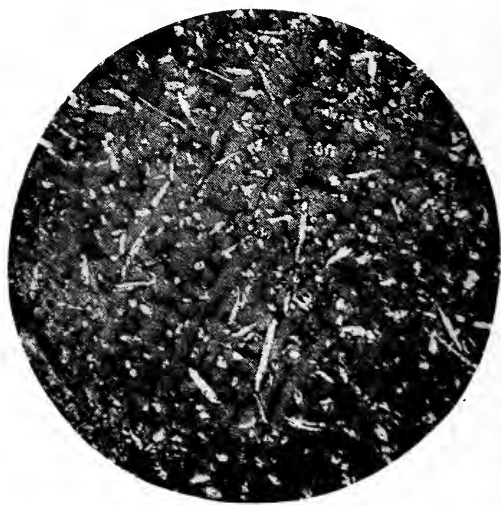


FIG. 61. ALLOY No. 49. x 40.
47.54% CR, 24.12% CU, 26.28% NI.
STAINED IN I IN KI.



FIG. 62. ALLOY NO. 50. x 40.
APPROX. 46.6% Cr, 11.4% Cu, 42.0% Ni.
STAINED IN I IN ALCOHOL.

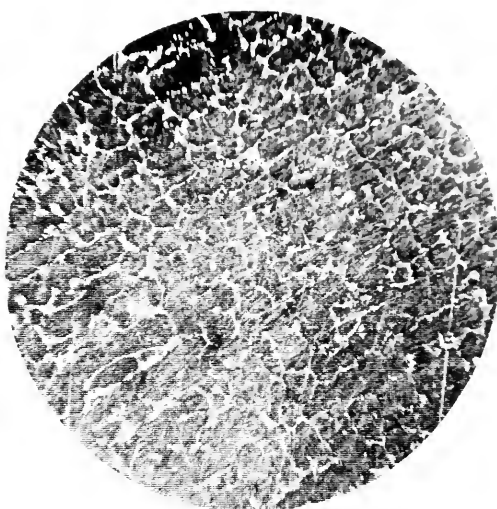


FIG. 63. ALLOY NO. 51. x 40.
57.40% Cr, 41.66% Ni.
ETCHED IN AQUA REGIA.

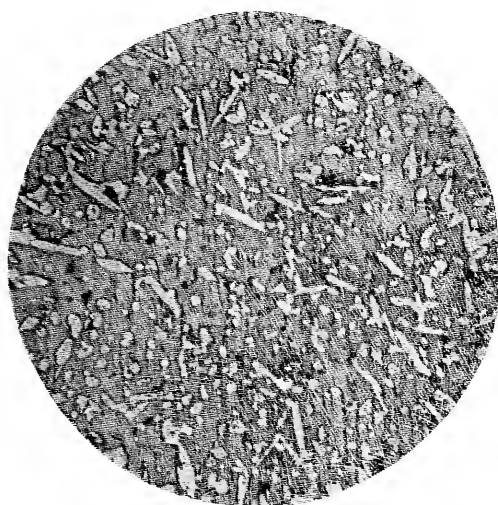


FIG. 64. ALLOY NO. 55. x 40.
APPROX. 56.6% Cr, 11.5% Cu, 31.9% Ni.
ETCHED IN AQUA REGIA.

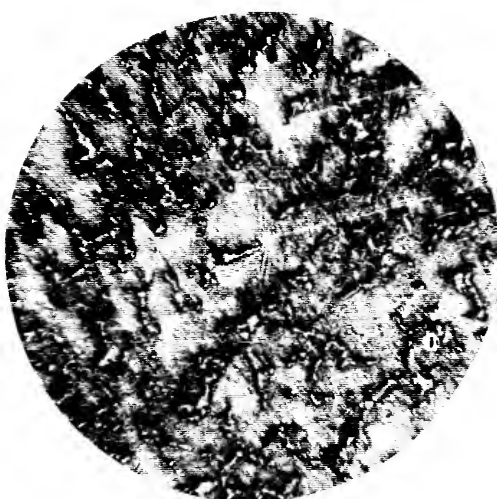


FIG. 65. ALLOY NO. 56. x 40.
APPROX. 57% Cr, 43% Ni.
ETCHED IN 1% FeCl_3 IN 1:1 HCl.
THEN STAINED IN I IN ALCOHOL.

APPENDIX

HISTORICAL REVIEW

In this review it is intended to give only the more important results of previous investigations and references to the original publications.

1. *Copper-Nickel Alloys*.—Christofle and Bouilhet* prepared alloys containing 50 per cent of copper and 50 per cent of nickel, and 85 per cent of copper and 15 per cent of nickel, and observed some of their properties.

In 1896 H. Gautier† made a more extensive study of these alloys. He determined their freezing points and concluded that they formed a definite chemical compound having the formula CuNi which melted at 1340 degrees C. The original paper was presented by H. Moissan.

Heycock and Neville‡ in their work on the “Complete Freezing-point Curves of Binary Alloys containing Silver or Copper together with Another Metal” tried the effect of the addition of small amounts of nickel upon the freezing point of copper and found that the freezing point was raised from 1080 to 1110 degrees C. by the addition of 4.5 per cent of nickel.

Kurnakoff and Schemtschny¶ prepared alloys from electrolytic copper and nickel, determined their freezing points, plotted the freezing-point curve, studied the structure of the different specimens, and pointed out certain similarities to the alloys of iron-copper, cobalt-copper, and copper-nickel. They took 1484 degrees C. as the melting point of nickel which is now known to be too high.

Guertler and Tammann§ in their investigation of the alloys of copper and nickel showed that there was no break in either the liquidus or solidus curves. This showed that these alloys do not form a definite chemical compound as had been claimed by H. Gautier. They made also both magnetic and microscopic examinations and showed the effect of heat on the magnetic properties as well as the effect of the rate of cooling on the grain and crystal size.

*Christofle and Bouilhet, *Bul. Soc. Chem.*, Vol. 26, p. 419, 1876.
Compt. rend., Vol. 83, p. 29, 1876.

†H. Gautier, *Compt. rend.*, Vol. 123, p. 172, 1896.

‡Heycock and Neville, *Philos. Trans.*, 189A, p. 25, 1897.

¶Kurnakoff and Schemtschny, *Z. anorg. Chem.*, Vol. 54, p. 149, 1907

§Guertler and Tammann, *Z. anorg. Chem.*, Vol. 52, p. 25, 1907.

The following year (1908) Victor E. Tafel* published the results of his studies of the constitution of the binary system copper-nickel. His work seems to be the best that has been published. For convenience his results are shown diagrammatically in Fig. 66. He obtained higher values for both the liquidus and the solidus curves than did Guertler and Tammann, but that may be attributed to the fact that they used nickel which contained a considerable amount of impurities (0.47 per cent Fe, 1.86 per cent Co.) which would lower the freezing points.

E. Vigouroux†, using pure metals especially free from cobalt, prepared a series of copper-nickel alloys, but he was unable to detect any indication of definite chemical compounds by chemical investigation or by a study of the electromotive forces in the cells $\text{Ni} - \frac{\text{N}}{1}$, $\text{NiSO}_4 - \text{CuNi}$ alloy and $\text{Cu} - \frac{\text{N}}{1}$, $\text{NiSO}_4 - \text{CuNi}$ alloy. His results by this method agree with those obtained by the cooling-curve method.

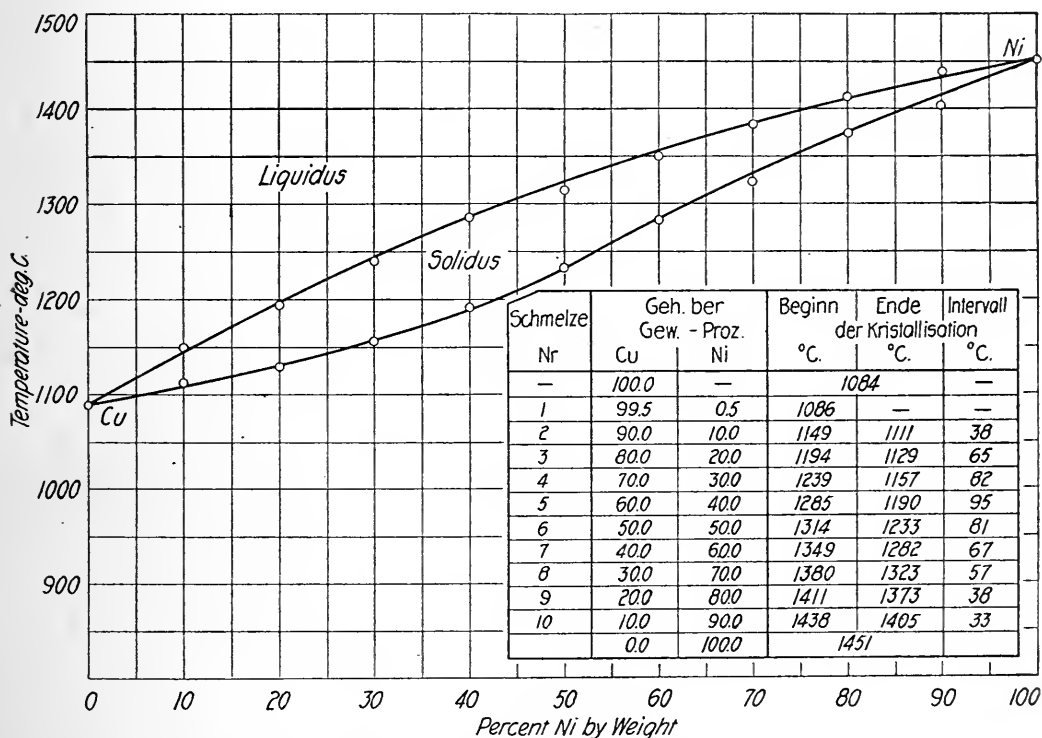


FIG. 66. COPPER-NICKEL EQUILIBRIUM DIAGRAM AFTER TAFEL.

*Victor E. Tafel, *Metallurgie*, Vol. 5, p. 348, 1908.

†E. Vigouroux, *Compt. rend.*, Vol. 159, p. 1378, 1909.

David H. Browne* secured U. S. patent 934,278 (Sept. 14, 1910) for the manufacture of nickel and copper-nickel alloys by electrically fusing compounds of the metals as sulfide matte with lime (CaO), forming calcium sulfide (CaS), sulfur dioxide (SO_2), and an alloy of the metals.

2. *Chromium-Copper Alloys*.—H. Moissan† prepared an alloy of chromium and copper which contained about 0.5 per cent of chromium. It was more resistant to humid air than was copper and took a beautiful polish.

H. Goldschmidt‡ has described an alloy of chromium and copper containing 10 per cent of chromium and having the color of copper, but being harder. The Goldschmidt Thermit Company§, 90 West Street, New York, now offers for sale an alloy of chromium-copper containing 10 per cent of chromium. The alloy is made by the aluminothermic method. This alloy is discussed more fully in Chapter II.

Hamilton and Smith§ heated chromium oxide and metallic copper in a carbon crucible and in the presence of carbon, by which process they obtained an alloy of gray-red color and of a hardness which placed it next to the alloys containing tungsten and molybdenum. The alloy gave the analysis: 88.18 per cent Cu, 3.22 per cent Cr, 1.35 per cent Fe, 2.38 per cent C, and 4.13 per cent gangue. The specific gravity was 8.3.

Binet de Jassonnix** stated that chromium dissolved in copper to the extent of about 1.6 per cent, but that on cooling, the chromium separated in a very finely divided condition.

G. Hindrichs†† made a more extensive study of the alloys of chromium and copper. He decided that the freezing point of copper was lowered about eight degrees by the addition of 0.5 per cent of chromium and that the maximum solubility of chromium in copper was 0.5 per cent. He, likewise, found that the freezing point of chromium was lowered from 1550 to about 1470 degrees C. by the addition of 5 per cent of copper and considered that the maximum solubility of copper in chromium was not over 5 per cent. From his researches it seems that there are two eutectic

*David H. Browne, C. A., Vol. 4, p. 41, 1910.

†H. Moissan, Compt. rend., Vol. 119, p. 185, 1894.

H. Moissan, Compt. rend., Vol. 122, p. 1302, 1896.

‡H. Goldschmidt, Liebigs Ann., Vol. 301, p. 25, 1898.

§Thermit Carbon-Free Metals, Pamphlet No. 20, 2nd ed., p. 23.

§Hamilton and Smith, Jour. Am. Chem. Soc., Vol. 23, p. 151, 1901.

**Binet de Jassonnix, Compt. rend., Vol. 144, p. 915, 1907.

††G. Hindrichs, Z. anorg. Chem., Vol. 59, p. 414, 1908.

points in the chromium-copper freezing point curve. His chromium-copper diagram has been reproduced in Fig. 67. He pointed out some of the difficulties in working with chromium or chromium-copper alloys. Chromium remains viscous after melting, attacks the crucibles, insulating tubes, etc., and has a strong tendency to oxidize. He was not able to get chromium and copper to separate into two well-defined layers.

From the foregoing paragraphs it may be seen that the different investigators have placed the solubility of chromium in copper at 0.5, 1.6, 3.22, and 10 per cents.

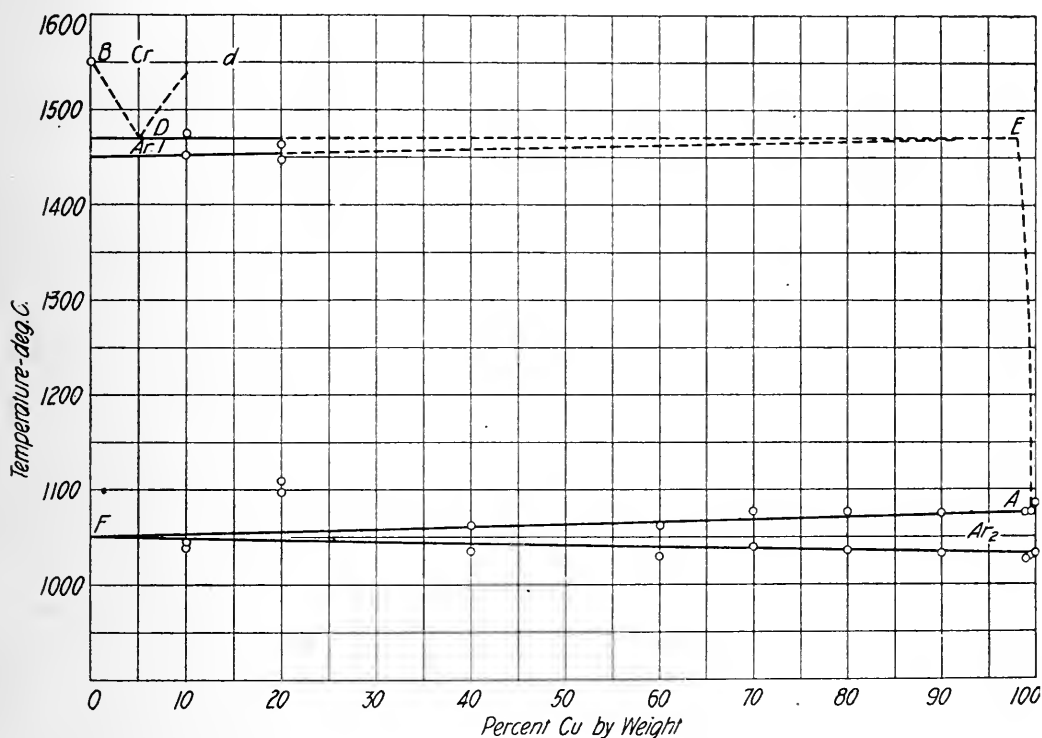


FIG. 67. COPPER-CHROMIUM EQUILIBRIUM DIAGRAM AFTER HINDRICHs.

3. *Chromium-Nickel Alloys*.—G. Voss* has investigated the alloys of chromium and nickel. His chromium-nickel diagram has been reproduced in Fig. 68. At the time he published his paper he stated that he was unable to find any published literature on the subject and at the present time he seems to be the only one who has published his researches. However, there have been extensive researches in the development of such alloys as "Nichrome", but these have been conducted in commercial laboratories and the re-

*G. Voss, *Z. anorg. Chem.*, Vol. 57, p. 34, 1908.

sults have not been published. Voss showed that the system consists of two series of solid solutions with a minimum freezing point of about 42 per cent of nickel. From a microscopic examination he concluded that the point represented a true eutectic, although he was not able to demonstrate the presence of a eutectic structure on either side of this point. He assumed the presence of a solution gap (Mischungslücke). On the other hand Guertler* concluded that the structure represented a condition of unstable equilibrium, which he termed a psuedoeutectic produced by the extreme viscosity of the chromium.

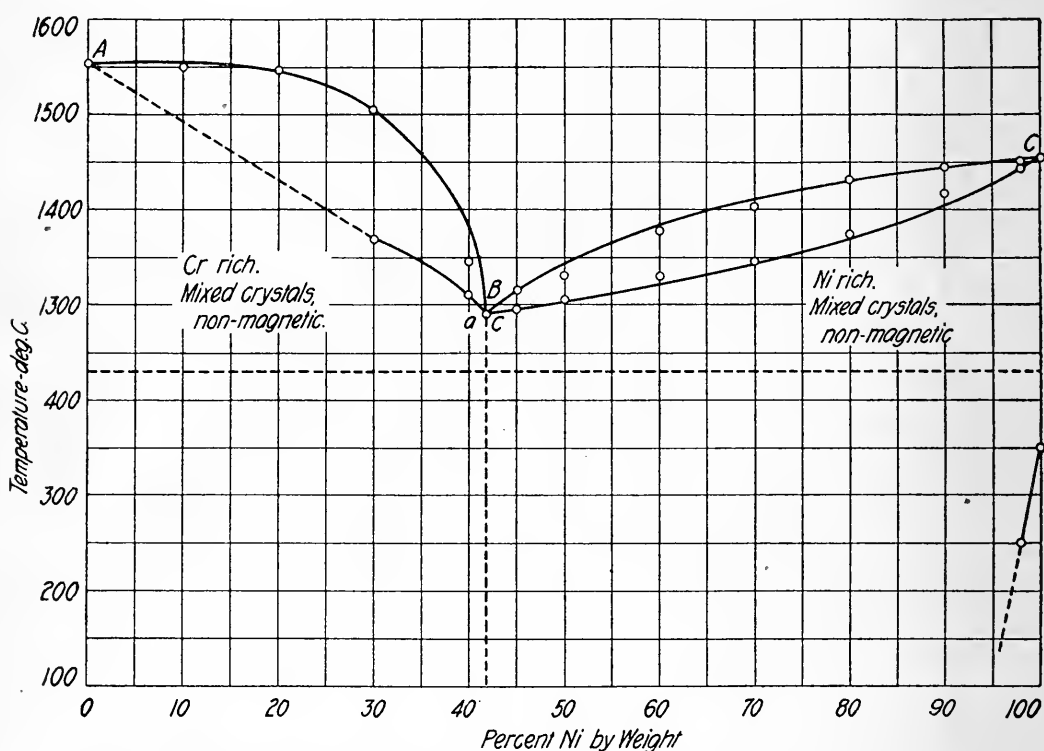


FIG. 68. NICKEL-CHROMIUM EQUILIBRIUM DIAGRAM AFTER VOSS.

To summarize, the binary alloys belong to three different classes: copper-nickel representing those which have continuous freezing-point curves, chromium-nickel representing those which have two series of solid solutions and a minimum freezing point, and chromium-copper those which have two eutectic points. The freezing-point curves for copper-nickel and for chromium-nickel seem to be pretty well established, but the exact location of a large part of the freezing-point curve for chromium-copper is unknown.

*Guertler, Metallographie, Vol. 1. Part I, p. 209, 1912.

4. *Ternary Alloys*.—The ternary alloys of chromium-copper-nickel have not been described, so far as is known to the writers, but four ternary systems which are somewhat closely related have been reported: copper-nickel-zinc by Victor E. Tafel,* copper-iron-nickel by R. Vogel,† copper-manganese-nickel by N. Parravano,‡ and cobalt-copper-nickel by Wahlert.§

*Victor E. Tafel, *Metallurgie*, Vol. 5, p. 413, 1908.

†R. Vogel, *Z. anorg. Chem.*, Vol. 67, p. 1, 1910.

‡N. Parravano, *Inter. Z. Metallographie*, Vol. 4, p. 171, 1913.

§Wahlert, *Oester. Z. Berg. Hüttenw.*,* Vol. 62, pp. 341-6, 357-61, 374-8, 392-5, and 406-10, 1914. *C.A.*, Vol. 8, p. 3549, 1914.

ACKNOWLEDGMENTS

In this work valuable assistance has been received from a large number of persons connected with the University of Illinois and the writer wishes to express his gratitude to those persons.

Professor D. F. McFarland has had charge of the entire investigation and has given much encouragement and assistance. Professor S. W. Parr has given many helpful suggestions. Professor H. F. Moore of the Department of Theoretical and Applied Mechanics directed the mechanical tests and criticised that part of the thesis. Mr. S. M. Hull made the copper and nickel determinations. Others to whom the writer is under obligations include Drs. Beal, Broderson and MacInnes, Messrs. Ford, Westhafer, McClelland, Rowland, Lee, and Brown and Miss Scott. The writer is also under obligations to the University of Illinois for a Fellowship in Chemistry during the two years that this investigation has been in progress.

VITA

The writer received his elementary education in the rural schools of Arkansas, Texas, and Oklahoma Territory. He received his secondary education in the Preparatory Department of the University of Oklahoma at Norman, Oklahoma, in the Agricultural and Mechanical College at Stillwater, Oklahoma, and in the Central State Normal School at Edmond, Oklahoma. He entered the University of Oklahoma in 1906 and graduated from that institution with the degree of B.A., 1910, and M.A., 1911, with majors in chemistry. He was instructor in Chemistry and Clerk of the Chemical Laboratory of the University of Oklahoma in 1910-1911 and in the summer sessions of 1910 and 1911. He became Food Analyst for the Kansas State Board of Health in 1911 with the rank of Assistant Professor at the University of Kansas. In 1913 he was placed in charge of the Food Laboratory. In September, 1913, he came to the University of Illinois as a Fellow in Chemistry and has remained in that position to the present time. His publications include:

“Note on the Standard Vanillin Solution for the Colorimetric Method for the Determination of Vanillin in Flavoring Extracts”, J. Ind. Eng. Chem. 5, (1913) p. 619.

Food Analysis Reports. Bulletin of the Kansas State Board of Health, 7, (1913) pp. 54-57, 70-74, 136-138, 150-153 and 167-173.

JUL 2 - 1917

LIBRARY OF CONGRESS



0 019 423 354